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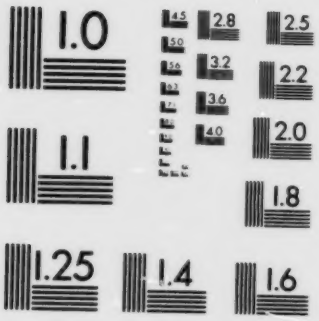

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DEVELOPMENT OF LABORATORY METHODOLOGY FOR EVALUATING EFFECTIVENESS OF ENGINEERED COVERS FOR REACTIVE TAILINGS

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Prepared for:

National Uranium Tailings Program

Prepared by:

R.S. Siwik, Contract Manager
NORANDA RESEARCH CENTRE

R.V. Nicholson, Ph.D.
BEAK CONSULTANTS LIMITED

J.E. Smith, M.Sc.
UNIVERSITY OF WATERLOO

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SUMMARY

This report presents a recommended laboratory methodology for evaluating the effectiveness of engineered covers for reactive tailings. The project was sponsored by the National Uranium Tailings Program. Sulphides, such as pyrite or pyrrhotite, in reactive tailings will oxidize in the presence of water and sufficient oxygen; bacterial activity can accelerate the reaction. One alternative to minimize oxidation of sulphides to acceptable levels would be to use fine-grained porous materials that maintains a high water content above the water table and limit the gaseous oxygen diffusion and infiltration.

The purpose of this investigation was to develop laboratory methods to evaluate the effectiveness of selected candidate materials as covers that would reduce acid generation in reactive tailings. The laboratory evaluation would serve as a screening process that would rate materials for later field trials.

A review of acid generation indicated the primary role of oxygen in the oxidation of reactive tailings. Oxidation of sulphides occurs predominantly in the unsaturated zone due to the availability of gaseous oxygen. Limiting the availability of gaseous oxygen is a key step in reducing acid generation in sulphide tailings.

A review of controlling processes indicated that the key parameters of concern are the oxygen diffusion coefficient, the volumetric water content, the soil-water pressure head, and the saturated hydraulic conductivity in the cover and in the tailings. The saturated hydraulic conductivity is less important because transport of dissolved oxygen in water moving through the tailings will result in minimal oxidation relative to oxidation with oxygen in the gas phase. Methods for assessment of water content and soil-water pressure head are available as standard methods that are presented in the literature review.

Standard laboratory methods for determining the rate of gaseous oxygen movement through selected porous materials are not available, and therefore equipment and procedures required development. A soil column apparatus was developed schematically. The device includes a constant oxygen supply, platinum micro-electrode oxygen detectors with depth, an oxygen sink consisting of either a platinum electrode or a ferrous sulphide bath, and a pressure plate device to simulate varying heights above the water table.

It is recommended that the laboratory apparatus and methods be evaluated, and a standard testing procedure established using porous materials that would be readily available and would represent candidate materials at a reactive tailings site. The results would be used to verify the proposed model that involves diffusion as the dominant transport mechanism with spatially variable diffusion characteristics within the cover material. The lab experiments could then be extended to include cover effectiveness with actual samples of tailings. The results of such experiments would than be used to design appropriate field tests for candidate cover materials. The recommended laboratory testing, model validation and subsequent field testing will provide a basis for the final design of cost-effective covers to reduce acid generation in, and the associated detrimental environmental impact from, reactive tailings.

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We wish to acknowledge the contributions of the following:

- Dr. R.W. Gillham, University of Waterloo
- K. Wheeland, Noranda Research Centre

This project was guided by Mr. Roy John, Scientific Authority.

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1.0 INTRODUCTION

1.1 Background

Sulphide tailings that are acid-generating occur over an area of approximately 9,000 hectares in Canada. A major concern of both the National Uranium Tailings Program (NUTP) and the Reactive Tailings and Waste Rock Program (RATS) is the prevention of oxidation of acid-generating sulphide tailings and waste rock. Four key parameters which the NUTP program (John, 1987) considered are temperature, bacterial population density, control of oxygen diffusion and subsequent transport of oxidized products by water movement. Control of temperature would not be practical. To date, limiting bacterial activity has required continual maintenance since bactericides need to be re-applied due to limited duration of product effectiveness. An effective method would be to eliminate the movement of water into a tailings pile by the means of an impervious cover, such as polyethylene geotextile membrane. However, the high costs associated with this cover strategy make investigation of other cover options attractive. One method of minimizing gaseous oxygen entry into the tailings is with underwater disposal. However, this technique is only practical at certain sites.

Limiting the oxygen penetration into the tailings with the use of cover materials to minimize oxygen penetration will reduce the rate of oxidation of sulphides. With a reduced rate of oxidation of sulphides, the natural buffering capacity of the tailings and associated geologic materials could reduce acidity and metal concentrations to acceptable levels.

1.2 Project Objective

A laboratory-scale methodology (see Appendix A for project proposal) is required to predict the effectiveness of alternative engineered soil covers in controlling oxygen diffusion and minimizing water movement into the tailings. This would provide cost-effective alternatives for field trial evaluation prior to full-scale implementation. This study addresses the need to ensure a proper development of laboratory equipment and methodology for evaluating effectiveness of engineered covers for reactive tailings.

1.3 Approach

An appropriate cover will reduce the rate of oxygen movement into the tailings by acting as an impediment to oxygen diffusion. Oxygen concentration with depth through a cover and into a reactive tailings deposit is presented schematically in Figure 1.1. The cover not only reduces the rate of movement but also reduces the availability of oxygen in the tailings where oxygen is consumed during sulphide mineral oxidation. The cover should be designed to minimize oxygen movement in the gas phase.

The design of an engineered cover will be limited by the availability of appropriate cost-effective materials. Candidate materials could consist of fine cohesionless silts, inert tailings or a composite of various available materials. A laboratory methodology is required to select materials, based on critical parameters, which will limit the rate of oxygen movement into the tailings. To determine the critical parameters, a review of acid generation in reactive tailings was conducted, including the role of dissolved oxygen, gaseous oxygen and water movement in the unsaturated zone. This review was used to identify the critical parameters and their interaction for the design of a laboratory-scale method of predicting the flux of oxygen through the cover and subsequent oxidation of sulphides.

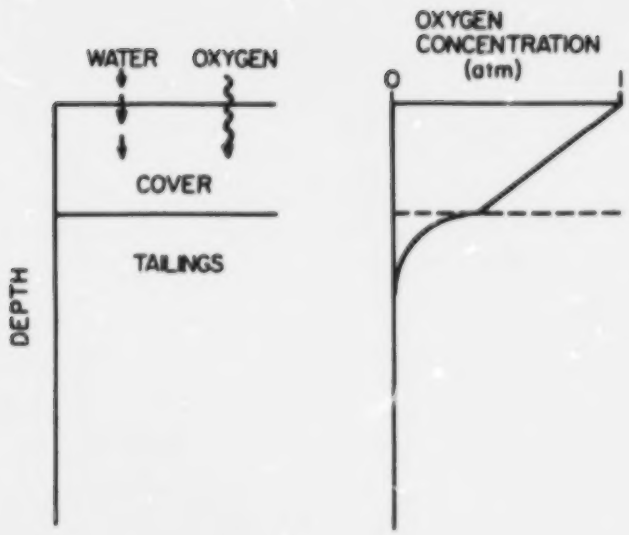


FIGURE 1.1: SCHEMATIC DIAGRAM SHOWING THE DISTRIBUTION OF OXYGEN CONCENTRATIONS WITH DEPTH THROUGH THE NON-REACTIVE COVER LAYER AND THE UNDERLYING REACTIVE TAILINGS

2.0 GENERAL THEORETICAL BACKGROUND

2.1 Acid Generation in Reactive Tailings

The rate of sulphide oxidation in pyritic tailings is critical to subsequent geochemical processes such as acidification and associated dissolution of metals. The acid which is generated indirectly controls the solubility of many constituents, most important of which are toxic metals in sulphide tailings. Because the reaction is favourable at the tailings surface and because the oxidation process is governed by kinetics, it is important to understand the controlling mechanisms involved. In this section, a brief overview of the controlling factors involved in the oxidation process is presented.

2.1.1 Oxidation Reactions

The two sulphides of primary concern in reactive tailings are pyrite and pyrrhotite. Although pyrrhotite is more reactive and will oxidize faster than pyrite, the chemical composition is similar to that of pyrite and the resulting acidification processes will be virtually the same. Pyrite is a ferrous sulphide mineral in which both elements are subject to oxidation. The complete oxidation of one pyrite molecule (FeS_2) involves the transfer of 15 electrons. The overall reaction consists of several intermediate steps. There is some question whether "complete" oxidation occurs in all environments. However, because there is not much evidence for the persistence of reaction intermediates, such as elemental sulphur, it is probable that complete oxidation is the most significant process in most environments. The pyrite oxidation cycle that leads to rapid production of acid is given schematically in Figure 2.1. Both pyrite and aqueous Fe^{2+} are oxidized by oxygen with and without bacterial mediation. Bacteria are most effective below a pH of 4.

The reactions are given stoichiometrically in the following equation:

$$FeS_2(s) + 15/4O_2 + 1/2H_2O \longrightarrow Fe^{3+} + 2SO_4^{2-} + H^+ \qquad (2.1)$$

or

$$FeS_2(s) + 7/2O_2 + H_2O \longrightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (2.2)$$

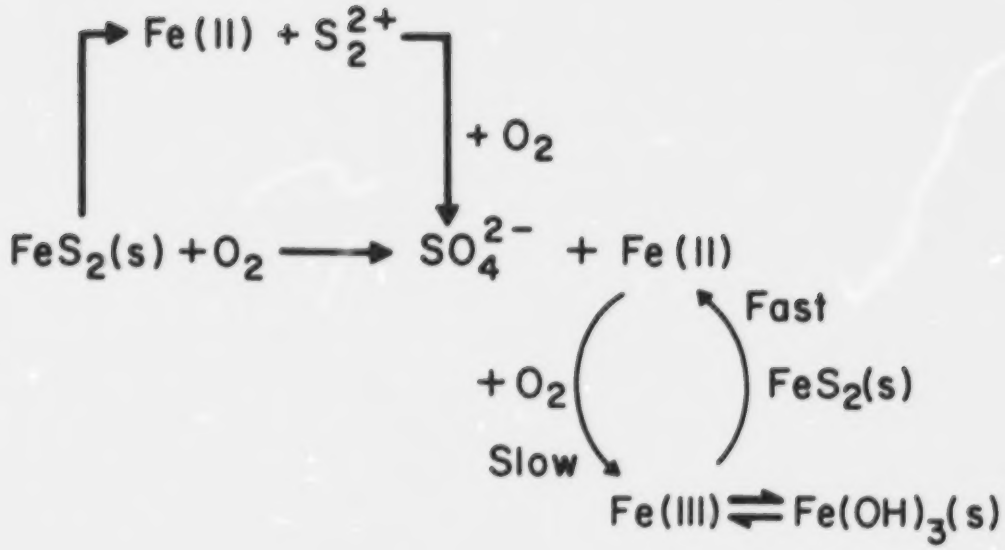


FIGURE 2.1: THE OXIDATION CYCLE FOR PYRITE SHOWING THE PRIMARY ROLE OF OXYGEN AND INTERMEDIATE ROLE OF Fe^{3+} AS OXIDANTS (after Stumm and Morgan, 1981)

When oxygen availability is not limited and when the pH is low, ferric iron (Fe^{3+}) will be produced and will further react with pyrite, as shown by the following equation:

$$14Fe^{3+} + FeS_2(s) + 8H_2O \longrightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.3)$$

At pH values of about 4 or greater, significant precipitation of ferric hydroxide will occur and result in further generation of acid as indicated by:

$$Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3(s) + 3H^+ \qquad (2.4)$$

This last reaction is reversible. When the pH decreases, the solubility of the ferric hydroxide increases and hence the extent of reaction (2.4) decreases, precluding it from contributing significantly to acidification under those conditions.

The total acidity produced during pyrite oxidation is that amount of H^+ when SO_4^{2-} and $Fe(OH)_3$ solid is formed. This would be the total acidity when a surface water environment is affected by seepage. The stoichiometry describing this process results from the addition of Equations 2.1 and 2.4, and gives the following:

$$FeS_2(s) + 15/4\ O_2 + 7/2\ H_2O \longrightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+ \qquad (2.5)$$

The overall mechanism of pyrite (or pyrrhotite) oxidation is not straight-forward. Inorganic and microbially-assisted oxidation play important roles in this process. However, one aspect is clear. Oxidation will not occur in the absence of oxygen. Even though Fe^{3+} plays an intermediate or catalytic role in oxidizing pyrite, Fe^{3+} would not be present without the initial reaction with oxygen. This suggests that oxygen availability and hence oxygen transport is the key issue to reactive tailings management. Other factors are involved in the overall rate of pyrite oxidation and subsequent acid generation, but it will be shown in the following sections that these are secondary to oxygen.

Of all naturally-occurring minerals, the weathering of pyrite and mechanisms involved have probably been the most closely studied. Much is known about the macroscopic factors controlling the rate of oxidation, but because of the complex nature of the reaction, little is understood with regard to the microscopic or mechanistic details.

Recent reviews of oxidation kinetics are given by Lowson (1982) and Nordstrom (1982). Some theories on surface related mechanisms are provided by Tributch and Bennett (1981a, 1981b), Goldhaber (1982) and by Nicholson et al. (1987). A brief summary of the known controls is given below. The major controlling factors include: (1) oxygen; (2) surface area; (3) temperature; (4) pH; (5) ferric iron concentration; and (6) bacterial population density.

2.1.2 Chemical Controls

The concentration of oxygen appears to control chemical oxidation rates according to a Langmuir-type adsorption isotherm. This behaviour implies that at low concentrations of oxygen, the rate is proportional to the partial pressure of oxygen gas (P_{O_2}) (first-order) while at high concentrations, the rate is independent of oxygen levels (zero-order) implying that the surface is completely saturated (Nicholson et al., 1987).

As with many mineral dissolution reactions, surface area plays a key role. The chemical rate of reaction is first-order with respect to surface area in the initial stages of the reaction. This order of reaction rate appears to change with time in neutral buffered environments, but this may be due to reaction coatings which form on the pyrite surface, altering the observed oxidation rates (Nicholson and Gillham, 1987).

The chemical reaction rate is affected by temperature. Using the Arrhenius concept, the activation energy has been determined under various conditions to be on the order of 80 to 90 kJ mol^{-1} for various conditions in the natural environment. This represents an approximate tripling of reaction rate for every $10^{o}C$ rise in temperature.

The solution pH can also control the chemical rate of oxidation. Although this has not been related to an actual mechanism, it has been observed that the rate (Smith et al., 1968) is a function of pH to a fractional power with the exponent in the range of zero to one. The observed trends indicate that the chemical rate of oxidation decreases with decreasing pH. This is consistent with what is known about the kinetics of ferrous iron oxidation in solution and it would be expected that pyrite would be more stable, chemically, in acidic solution (i.e., in the absence of bacteria).

The concentration of ferric iron (Fe^{3+}) in solution also affects the oxidation rate. Ferric iron reacts with the pyrite surface to form sulphate and ferrous iron. This reaction is relatively rapid and depends on the concentration of Fe^{3+}, as well as available surface area of pyrite. In most environments, Fe^{3+} concentrations will be limited to low values by the solubility of $Fe(OH)_3$ and therefore will not represent an important source of oxidant. However, under acidic conditions, Fe^{3+} concentration levels can be high and may provide a significant contribution to reaction with the pyrite surface. Furthermore, in microbially-active systems, relatively large quantities of Fe^{3+} are rapidly generated, thereby providing a greater source of oxidant. It should be noted that this Fe^{3+} is depleted rapidly by reaction with the pyrite surface. Observation of significant (FeIII/FeII) ratios (greater than 0.01) in tailings leachate suggests that microbial activity is a significant factor.

2.1.3 Bacterially-assisted Oxidation

The role of acidophilic bacteria in the catalysis of pyrite oxidation has been well documented (Lundgren and Silver, 1980; SENES, 1984). While the role of various factors has been shown above with respect to chemical oxidation rates, these factors have different effects on the rate of oxidation resulting from bacterial action. Thiobacillus ferrooxidans is the organism responsible for catalysing the oxidation of Fe^{2+} to Fe^{3+}; the Fe^{3+} catalyzes the reaction inorganically at the pyrite surface. Bacteria also appear to catalyze the oxidation directly on the pyrite surface. Regardless of the mechanism, however, catalysis is the key role played by bacteria.

When bacteria are the dominant control on reaction rates, the surface area of pyrite appears to play a similar role to that for chemical oxidation. The effect of oxygen concentration may not be of significance, however, until levels below about 1 to 5% of atmospheric values. The dependence on oxygen concentration below these levels appear to be linear. Because bacterial metabolism is involved, the temperature range has an optimal level (approx. $30^{\circ}C$) with declining rates on either side of this value. Similar behaviour is observed for variations in pH with optimal values in the range of 3.0 to 3.5. Most evidence suggests that bacterial catalysis of the oxidation reaction is insignificant at pH values above about 4 to 5 (Arkesteyn, 1980). This implies that the acidification of pore water associated with pyritic material is initiated mainly through chemical processes for the pH range of neutral to about 5.

2.1.4 The Vadose Zone

The zone of active oxidation occurs in the vadose (unsaturated) zone above the water table. Oxygen availability and pyrite oxidation kinetics are the factors that determine the depth of the zone of active oxidation and the resulting acid production rates.

The oxidation of sulphide minerals is practically limited to this zone because of the restraints on oxygen transport in the subsurface which will be expanded upon in a later section. The following discussion addresses the practical implications of acid generation above the water table.

The actual thickness (depth interval) of the active oxidation zone depends on the relative rate of oxygen transport into the tailings to the rate of oxygen consumption during pyrite oxidation. When the rate of oxygen movement is fast compared to the rate of consumption, then the zone of active oxidation will be extended. When the rate of consumption is closer in value to the rate of movement, the active zone is compressed (SENES-BEAK, 1986). There is evidence in some environments that this active zone can be limited to a few centimetres. The actual rate of acid production is directly linked to the rate of oxygen movement or oxygen flux through the tailings. The depth of oxygen penetration alone is not necessarily indicative of the rate of acid production in the tailings.

The thickness of the zone of active oxidation does, however, have important implications for the precise chemistry of the resulting pore water in that zone which in turn can affect the kinetics of pyrite oxidation (i.e., pH changes affecting microbial activity, inhibiting concentrations of metals). There would also be some effects on the precipitation and dissolution of certain mineral phases. However, in practical terms, the thickness of the oxidation zone does not control the acid generation rate in the vadose zone. The rate of oxygen generation in this zone is limited to the rate of oxygen entering the tailings surface. The rate that oxygen enters the tailings at the surface will, therefore, represent the maximum rate of oxidation.

2.1.5 The Role of Oxygen in Acid Generation

The preceding discussion indicates that a number of factors influence the rate of oxidation in reactive tailings and the subsequent rate of acid generation in this

environment. The key issue, however, that overrides all other factors is the availability of oxygen for reaction with sulphide minerals. Whether or not bacteria are available, and whatever the grain size characteristics of the sulphide minerals, and regardless of whether or not the porewater is buffered by carbonate material, oxidation will not occur if oxygen is unavailable.

Other factors controlling the rate of oxidation provide a basis for calculating these rates when the characteristics of the reactive tailings environment are known. These predicted rates are necessary to precisely model oxygen transport and consumption within the tailings system. The oxygen concentration at a particular location within the tailings is one parameter that is required to predict the oxidation rates. However, if oxygen supply is restricted at the tailings surface, and movement of oxygen into the tailings is reduced, then the subsequent rate of oxidation and acid generation will also be reduced. This important role for oxygen provides a focus for any remedial action designs for reactive tailings.

2.2 Mass Transport in Unsaturated Soils

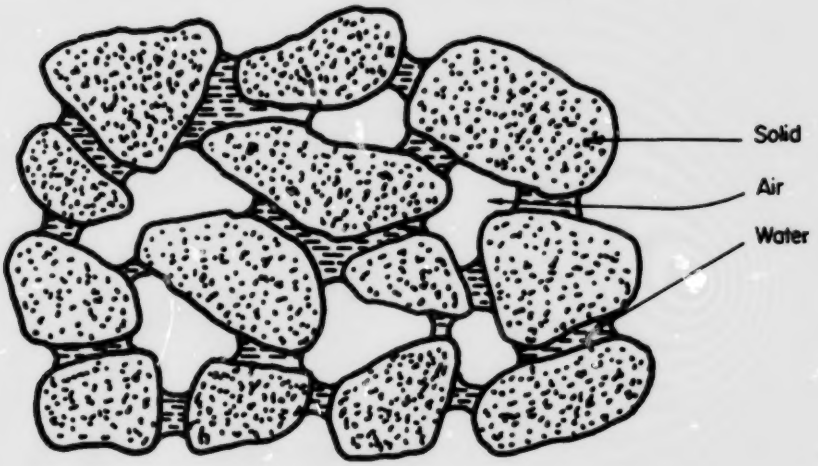
2.2.1 Water Movement

One of the fundamental relationships that describes fluid flow through porous media is Darcy's Law:

$$v = -k \frac{dh}{dx} \qquad (2.6)$$

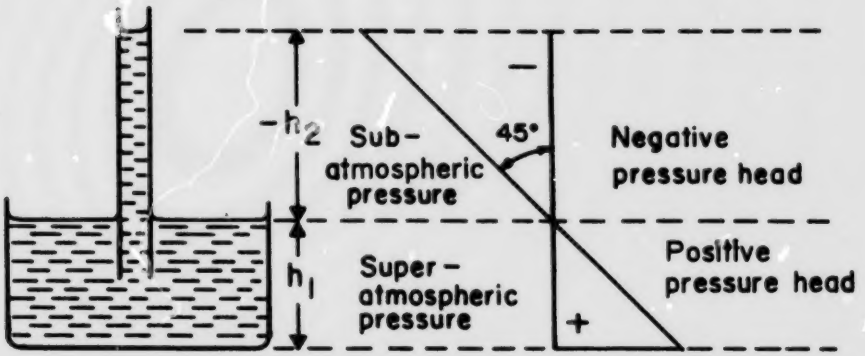
Darcy's Law is a linear relationship between the specific discharge (v; $m^3\ m^{-2}\ s^{-1}$) and the driving force, the hydraulic gradient (dh/dx), with the proportionality coefficient being the hydraulic conductivity (k). This relationship holds true for both saturated and unsaturated conditions.

Whereas the water in a saturated soil is under positive pressures relative to atmospheric (gauge pressure), the water in an unsaturated soil is held in the pores under negative pressures (tension) caused by the surface tension between water and air (see Figure 2.2). This soil-water pressure head varies with water content (see Figure 2.3) because smaller



Water in an unsaturated coarse-textured soil.

(a)



(b)

FIGURE 2.2: WATER IS HELD IN UNSATURATED POROUS MEDIA UNDER NEGATIVE PRESSURE HEAD (after Hillel, 1980)

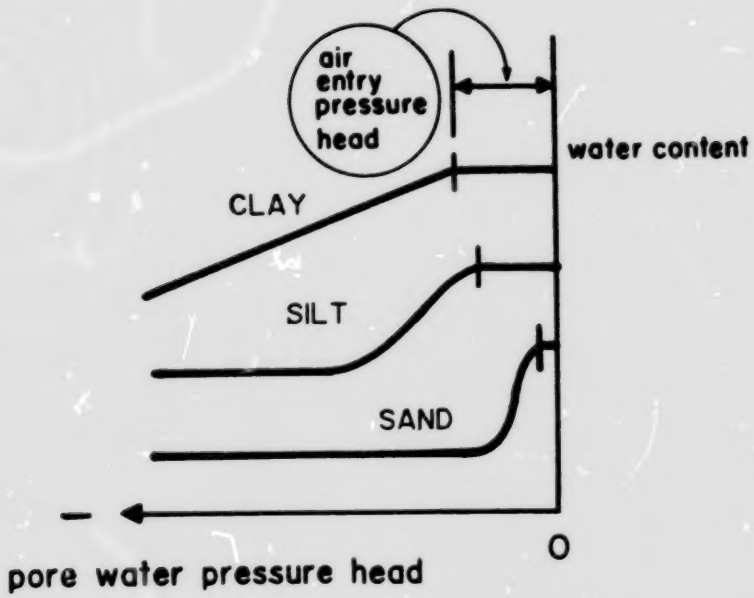


FIGURE 2.3: SOIL-WATER CONTENT VERSUS PRESSURE HEAD (IGNORING HYSTERISIS) (after Freeze and Cherry, 1979)
a) uniform sand
b) silty sand
c) silty clay

pores hold water under greater tension than larger pores, due to the greater curvature of the water menisci. Figure 2.4 shows the result of this phenomena relative to the water table. In the saturated soil, the hydraulic conductivity (k) is a constant; however, in the unsaturated zone, k varies with pore water pressure head (p_w) (see Figure 2.5) and thus with the water content (w). As the pore water pressure head becomes more negative (drier soil), more pores drain and no longer contribute to the flow of water, thereby reducing the hydraulic conductivity of the soil.

A clearer conceptual appreciation of the difference between water flow in saturated and unsaturated soil can be achieved by inspecting Figure 2.5. This diagram shows the variation of the hydraulic conductivity (k), the pore water pressure head (or simply noted as pressure head) (p_w) and the water content (w), along a horizontal soil core conducting water under steady-state conditions.

The non-linear characteristics of the unsaturated flow system result in it being more difficult to accurately model water flux.

The equation that describes unsaturated soil water flow is:

$$\frac{\partial w}{\partial t} = \frac{\partial}{\partial x}\left[k(p_w) \frac{\partial p_w}{\partial x} \right] \qquad (2.7)$$

where:
- w = the volumetric water content
- p_w = the pressure head
- k = the unsaturated hydraulic conductivity.

Traditionally, the subject of unsaturated flow of water in soil has been dealt with by subdivision into narrower topics with infiltration, drainage and evapotranspiration being prominent. The following is a brief discussion of these three topics for uniform soil profiles (such as a single layer engineered soil cover). The textbooks by Hillel (1980a, b) provide a more in-depth discussion than will be presented here and are good sources of further references on these topics.

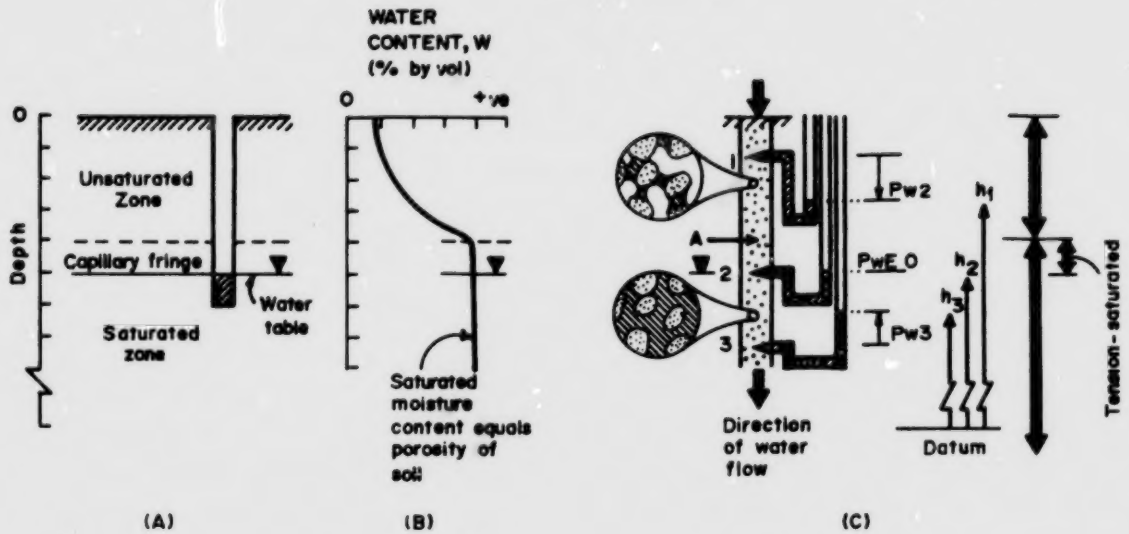


FIGURE 2.4: AN EXAMPLE OF WATER CONTENT, PRESSURE HEAD AND HYDRAULIC HEAD FOR THE CASE OF RECHARGE TO A WATER TABLE (after Freeze and Cherry, 1979)

a) saturated and unsaturated zones
b) profile of moisture content versus depth
c) pressure head and hydraulic-head relationships; insets: water retention under pressure heads less than (top) and greater than (bottom) atmosphere

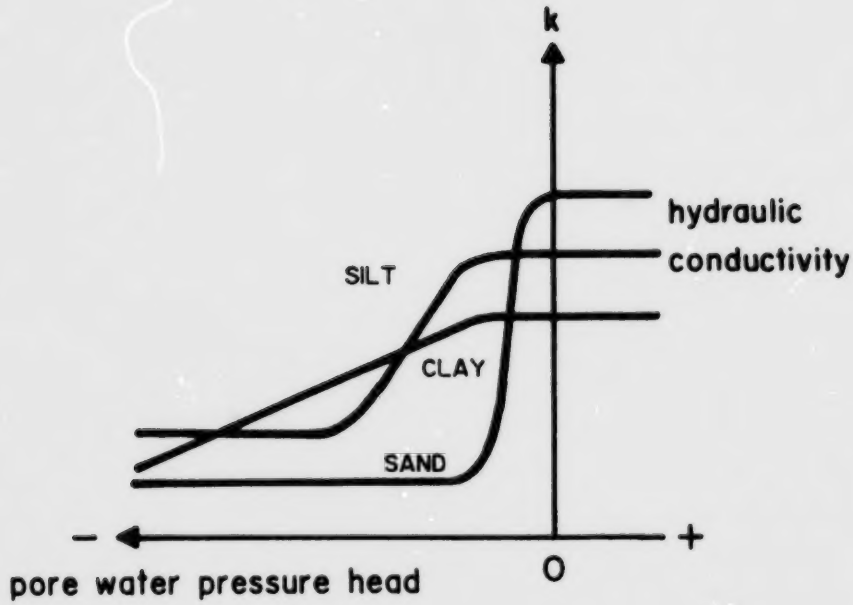


FIGURE 2.5: HYDRAULIC CONDUCTIVITY VERSUS PORE-WATER PRESSURE HEAD (after Freeze and Cherry, 1979)

a) uniform sand
b) silty sand
c) silty clay

The rate at which water infiltrates into an unsaturated soil when water is applied to the soil surface at atmospheric pressure (infinitesimal ponding depth) is termed the infiltrability. If water is ponded to some depth on the surface of the soil, the infiltration rate will exceed the infiltrability. The infiltration rate will be less than the infiltrability if the water is applied at a rate lower than the infiltrability. Even when water is applied at atmospheric pressure, the infiltrability is not constant. As shown in Figure 2.6, the infiltrability decreases with time until, at long time, a steady infiltrability value is approached. A further complication arises in that the infiltrability depends on the initial water content of the soil as shown in Figure 2.7. For the purpose of introducing concepts of infiltration into a uniform soil layer, we will restrict the remainder of the section to infiltration of shallow ponded water on the soil surface. Figure 2.8 shows plots of hydraulic head and degree of saturation versus depth for continuous shallow ponding of water on the soil surface.

As the wetting front reaches a given depth in the soil, the hydraulic head increases with time, as does the degree of saturation. When time is relatively large, the hydraulic gradient approaches the unit gradient with the pressure head equal to zero throughout the profile and the change in hydraulic head is due to the change in elevation head only. At that time, the water flux density (specific discharge) is numerically equal to the hydraulic conductivity. Under these conditions water will not infiltrate at a rate greater than the hydraulic conductivity unless significant ponding occurs on the surface.

When water is applied to the soil surface for a relatively short period of time, the water redistributes in the soil profile as shown in Figure 2.9. The actual water content at a given depth and time is dependent on the soil water characteristic curve of the particular soil in question. This type of infiltration and redistribution would occur in a tailings cover after a rainfall event.

The changing soil moisture distribution during drainage of a uniform soil profile that is initially saturated is shown in Figure 2.10. Comparing the sand, loam and clay soils, we see that fine grained soils maintain higher water contents (therefore lower air filled porosity) than coarse grained soils drained for the same period of time. This is due to both the lower conductivity and smaller pores in the clay soil.

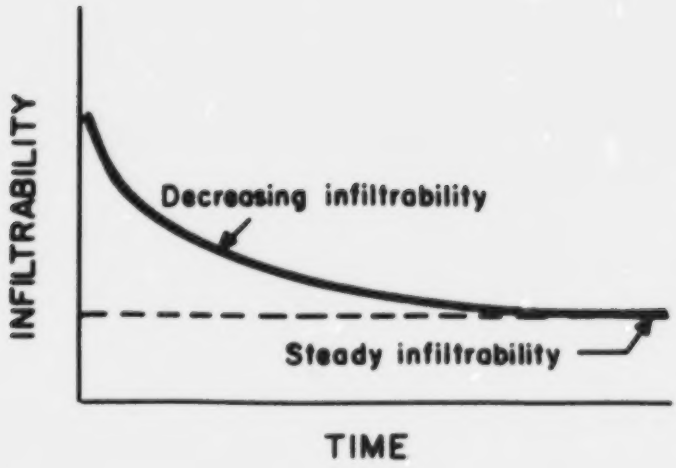


FIGURE 2.6: INFILTRABILITY VERSUS TIME (after Hillel, 1980b)

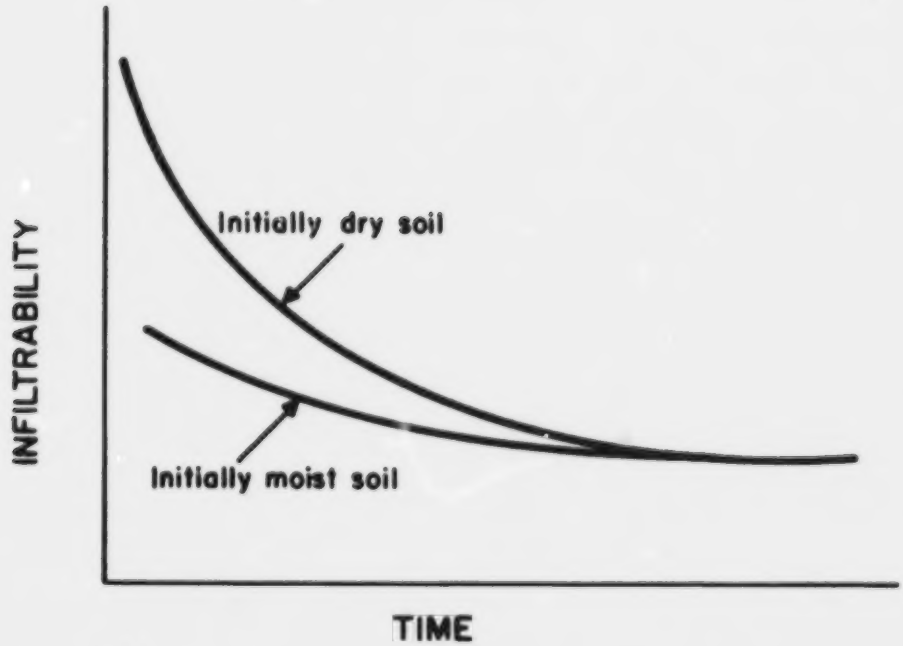


FIGURE 2.7: INFILTRABILITY VERSUS TIME FOR AN INITIALLY DRY AND INITIALLY WET SOIL (after Hillel, 1980b)

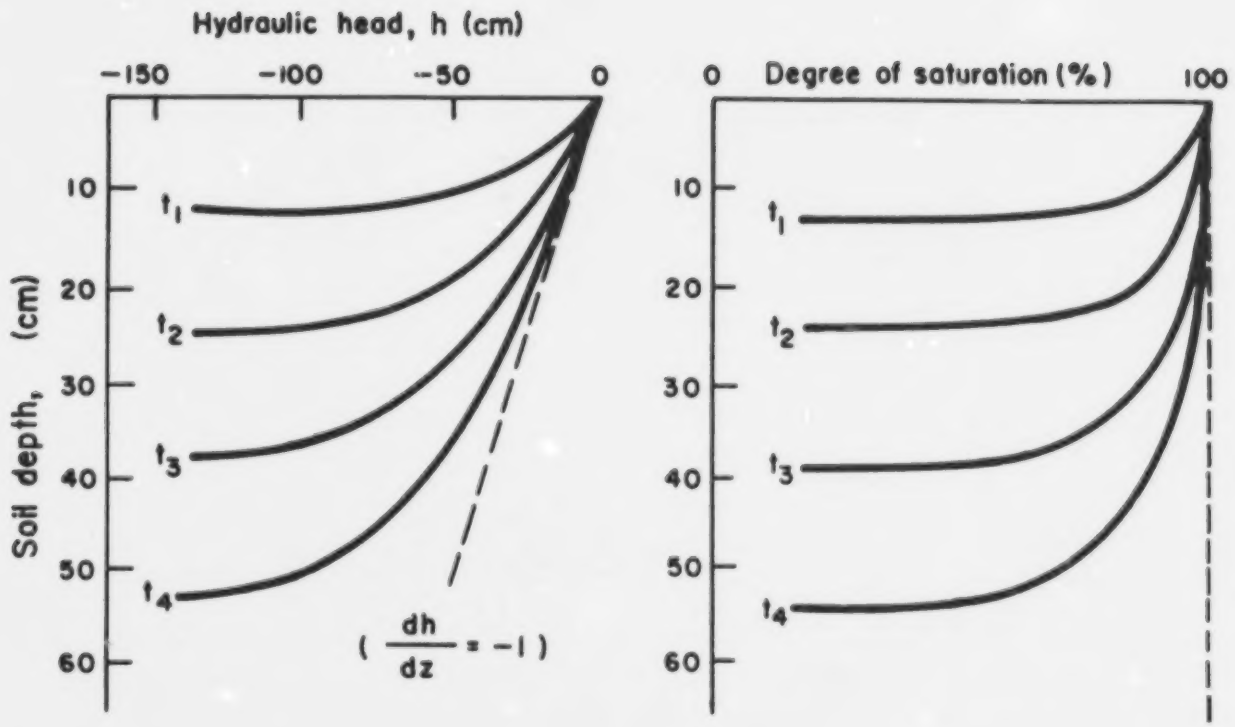


FIGURE 2.8: WATER CONTENT PROFILES (AT RIGHT) AND HYDRAULIC HEAD PROFILES (AT LEFT) AT DIFFERENT TIMES DURING INFILTRATION (after Hillel, 1980b)

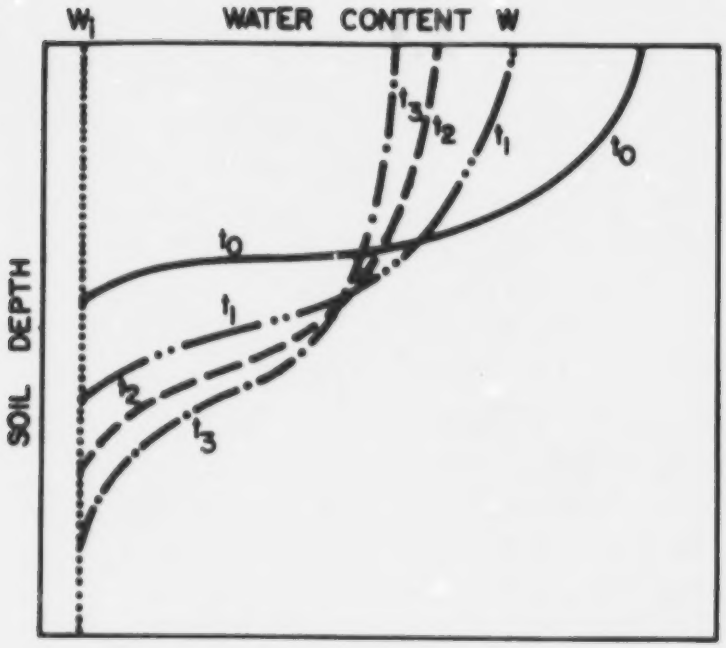


FIGURE 2.9: THE CHANGING MOISTURE PROFILE IN A MEDIUM-TEXTURED SOIL DURING REDISTRIBUTION FOLLOWING AN IRRIGATION. The moisture profiles shown are for T = 0, 1, 4 and 14 days after irrigation. w_i is pre-irrigation (antecedent) water content (after Hillel, 1980b).

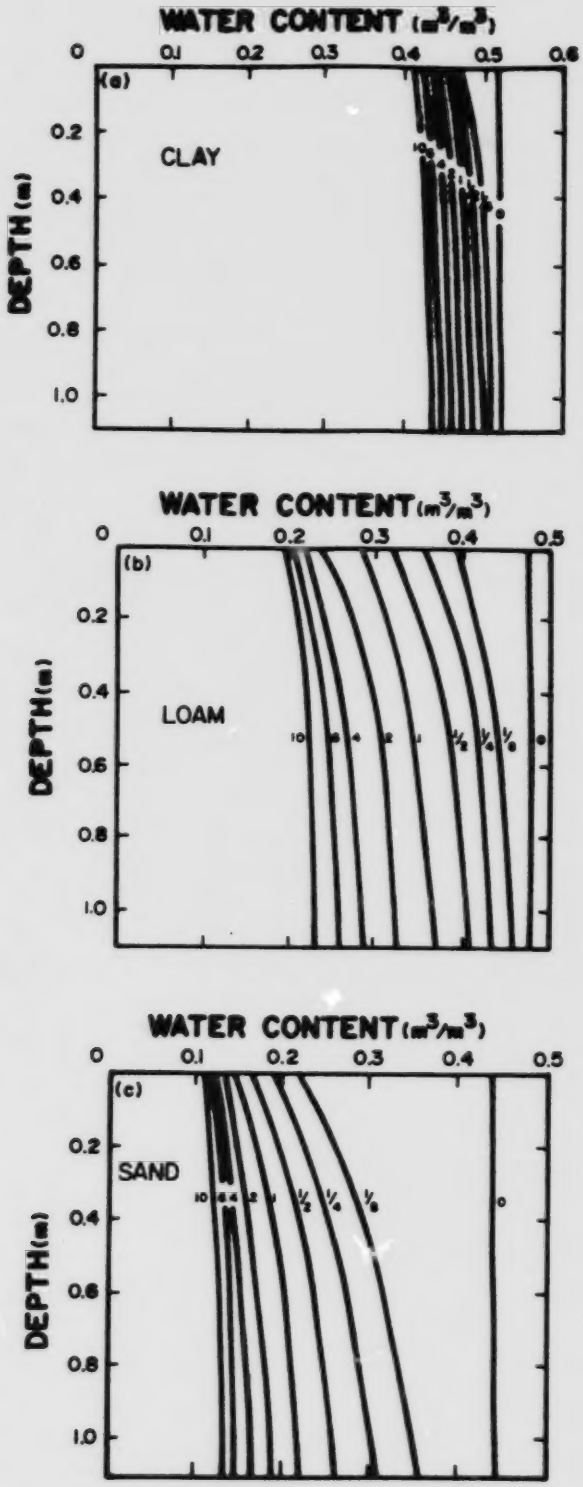


FIGURE 2.10: THE CHANGING SOIL MOISTURE DISTRIBUTION DURING DRAINAGE FROM INITIALLY-SATURATED UNIFORM PROFILES OF (A) CLAY, (B) LOAM, AND (C) SAND. THE NUMBERS INDICATE DURATION OF THE PROCESS (DAYS) (after Hillel, 1980b)

This relationship between soil textures is also apparent in plots of volumetric water content versus time at a depth of 41 cm (arbitrary) shown in Figure 2.11. Figure 2.11 also shows the additional effect of simultaneous evaporation from the soil surface. Tailings covers would be saturated in the spring during and immediately after snow-melt, and would likely exhibit the type of drainage shown in Figures 2.10 and 2.11.

The water content versus soil depth profile caused by evaporation at a bare soil surface is shown in Figure 2.12. If vegetation was present, the plant roots would be extracting water from the soil to be transpired to the atmosphere. The combined effect of evaporation and transpiration is termed evapotranspiration. The presence of vegetation results in a greater loss of water from the soil and drying of the soil to a greater depth, dependent on plant type and time of year.

Modelling of water flow in unsaturated soils is complicated by the non-linear nature of the interrelationships of the soil water properties, and by the fact that steady-state flow conditions are seldom achieved in the field.

2.2.2 Oxygen Movement

There are a number of potential mechanisms contributing to the mass transport of oxygen through an unsaturated porous medium. These processes can generally be classified as either diffusive or advective transfer. Advective and diffusive transfer occur both in the gas phase and as a dissolved constituent in porewater, and thus transport can occur in both phases.

Diffusion is the result of random movement of particles due to their kinetic energy. In systems containing gradients in chemical potential (i.e., concentration), diffusion will induce a mass flux. When the oxygen concentration in a surficial porous medium is lower than the atmospheric level, a net diffusive mass flux of oxygen into the deposit results. Diffusion occurs in both the liquid and gas phases; however, because the diffusivity of air is four orders of magnitude greater than that of water, the mass flux in the gas phase is usually dominant in a deposit containing interconnecting gas-filled pores.

Advective transfer of oxygen in the gas phase can occur as a result of barometric pumping, turbulent flow due to wind action, and gas removal by plant roots resulting in

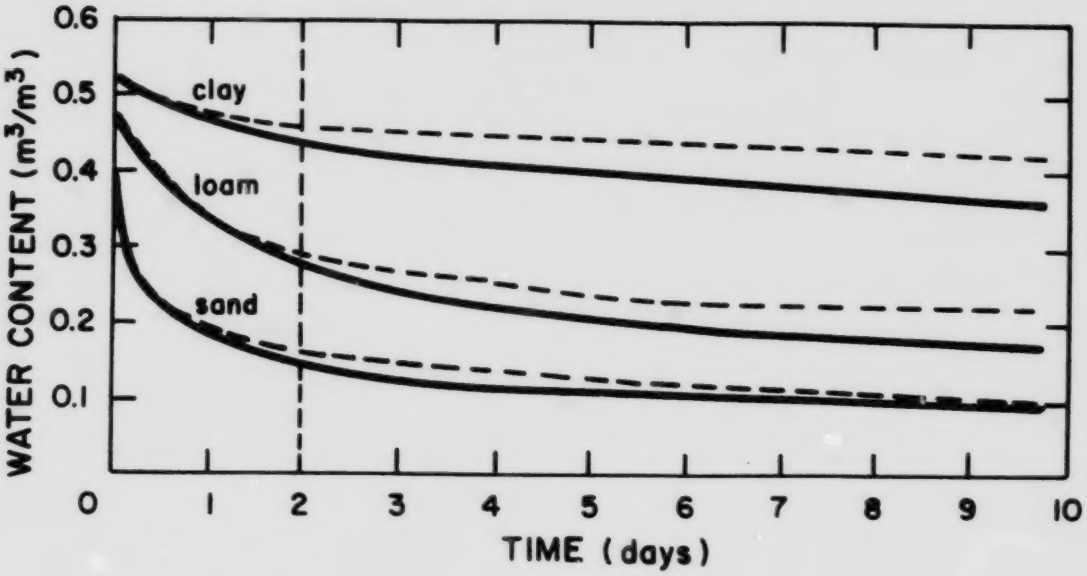


FIGURE 2.11: WATER CONTENT (W) AT DEPTH OF 41 CM AS FUNCTION OF TIME IN INITIALLY-SATURATED UNIFORM PROFILES OF SAND, LOAM, AND CLAY. DASHED LINES-DRAINAGE WITHOUT EVAPORATION; SOLID LINES-SIMULTANEOUS DRAINAGE AND EVAPORATION (after Hillel, 1980b)

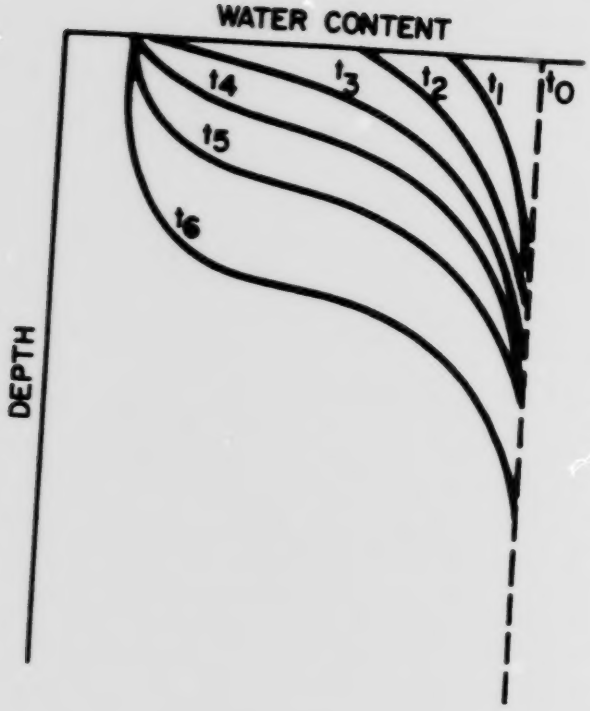


FIGURE 2.12: WATER CONTENT VERSUS DEPTH SHOWN FOR VARIOUS TIMES DURING EVAPORATION FROM AN INITIALLY SATURATED SOIL

inflow of atmospheric gas at the surface to replenish removed volumes. The relative contribution of these factors, however, is likely to be quite small, except for a thin zone at the surface in sandy to silty tailings (e.g., Kimball and Lemon, 1971).

In natural soils that are well-drained, it is expected that most of the gaseous exchange between soil gas and the atmosphere is by gaseous diffusion (Evans, 1965; Kimball and Lemon, 1971; Kirkham and Powers, 1972). Under other conditions, where pore spaces are almost entirely filled with water (i.e., almost saturated), the flux of oxygen will be low and limited by the lower diffusivity in water. Nicholson (1984) found that the infiltration of dissolved oxygen could become an important or dominant component of the downward oxygen flux if diffusion through the pore network is sufficiently restricted by high water content. In either case, calculations can be performed to determine the approximate relative importance of each of these mechanisms to oxygen transport.

2.2.3 Oxygen Transport Model

A number of models have been used to describe oxygen transport through a porous medium. The common basis for these is the inclusion of a diffusion term to describe oxygen movement. Models have been developed to describe oxygen transport into reactive tailings (Nicholson, 1984; SENES-BEAK, 1986) and into ore leaching piles (Cathles and Apps, 1975). The emphasis on transport mechanisms differs for each of these cases, but the fundamental principles are the same. The following discussion introduces a relatively comprehensive model for oxygen transport that could be applied to tailings covers and/or laboratory experiments designed to determine the behaviour of the potential cover materials.

Oxygen transport is assumed to occur as a result of diffusion through the gas phase and as dissolved water infiltrating (at rate q). The differential equation describing oxygen movement can be written as:

$$D_e E \frac{\partial^2 C}{\partial x^2} - \frac{q \partial C^*}{\partial x} = E \frac{\partial C}{\partial t} + \rho_w n \frac{\partial C^*}{\partial t} + G \qquad (2.8)$$

where: D_e is the effective diffusion coefficient of oxygen,
E is the air-filled porosity,
q is the infiltration rate of water,

C is the concentration of oxygen in the gas phase,
C* is the concentration of dissolved oxygen in the water,
x is depth,
$_w$ is the density of water,
G is the reaction term for oxygen (possibly a function of C),
n is the porosity, and
t is time.

Assuming that oxygen dissolution in water is an equilibrium process, then the expression can be simplified to:

$$D_e E \frac{\partial^2 C}{\partial x^2} - \frac{q}{K_w} \frac{\partial C}{\partial x} - G = \left[E + \frac{\rho_w n}{K_w} \right] \frac{\partial C}{\partial t} \qquad (2.9)$$

in which K_w is the dissolution constant for oxygen in water (Henry's Law Constant). This equation is simplified at steady-state when the right-hand side is equal to zero.

This equation describes the oxygen movement into tailings or other material which consumes oxygen. When oxygen migrates through a cover material that does not consume oxygen, G = 0 and an appropriate solution can be found.

2.3 Theoretical Limits to Oxygen Transport

Oxygen movement within the porous medium is controlled by both the infiltration of water containing dissolved oxygen and the diffusion of oxygen in the gas phase and water phase of the pores. It is possible to estimate both the maximum and minimum rates of oxygen movement through a cover material on tailings. The flux of oxygen through such a cover can be estimated for both diffusion and advection separately to show the relative influence of each process.

Oxygen flux by advection (entering as dissolved oxygen with the natural infiltration) in water is calculated in the following way.

$$F_a = qC^* \qquad (2.10)$$

where: F_a is the advective flux of oxygen (in mass per unit area per unit time),
q is the rate of infiltration through the cover (length per time), and
C^* is the concentration of dissolved oxygen in the infiltrating water (mass per unit volume).

The average annual rate of infiltration is usually known within reasonable limits. For instance, in northern Ontario, infiltration in a vegetated area would likely be on the order of 0.01 to 0.25 m a^{-1} (i.e., $m^3\ m^{-2}\ a^{-1}$). Higher rates of infiltration are, of course, possible, but an absolute upper maximum equal to the amount of annual precipitation must hold. With a maximum precipitation of about 1.0 m a^{-1}, it is not likely that annual cumulative infiltration will be greater than about 0.5 m a^{-1}. For the purpose of the following calculations, the range of infiltration values is assumed to be 0.01 to 0.10 m a^{-1}. The value of C^* (dissolved oxygen concentration) is constant for a specified temperature. Therefore, the flux of oxygen through the cover, due to transport in water, can be calculated within at least an order of magnitude range.

When oxygen is consumed rapidly in the underlying tailings, oxygen diffusion through a cover material can be described by steady-state diffusion (Nicholson et al., 1987). When the tailings consume oxygen at a moderate to high rate such as that expected in reactive tailings, then the flux relationship reduces to:

$$F_d = (D_e/L)\, C_o \qquad (2.11)$$

where: F_d is the flux of oxygen,
D_e is the effective diffusion coefficient of oxygen in gas-filled pore spaces,
L is the thickness of the cover, and
C_o is the concentration of oxygen in the atmosphere.

This relationship represents Fick's first law when the concentration of oxygen at the bottom of the cover is zero. It is convenient to take the ratio of D_e/L as a mass transfer term that varies over a wide range of values. The equation can then be used to show the numerical relationship between the diffusive flux F_d and the mass transfer value (D_e/L). It is known that the value of D_e will vary from about $1x10^2$ to $1x10^{-2}$ $m^2\ a^{-1}$ for diffusion through air to diffusion through water, respectively. The effective diffusion coefficient in a water-saturated porous medium may be somewhat lower than $1x10^{-2}$ m^2

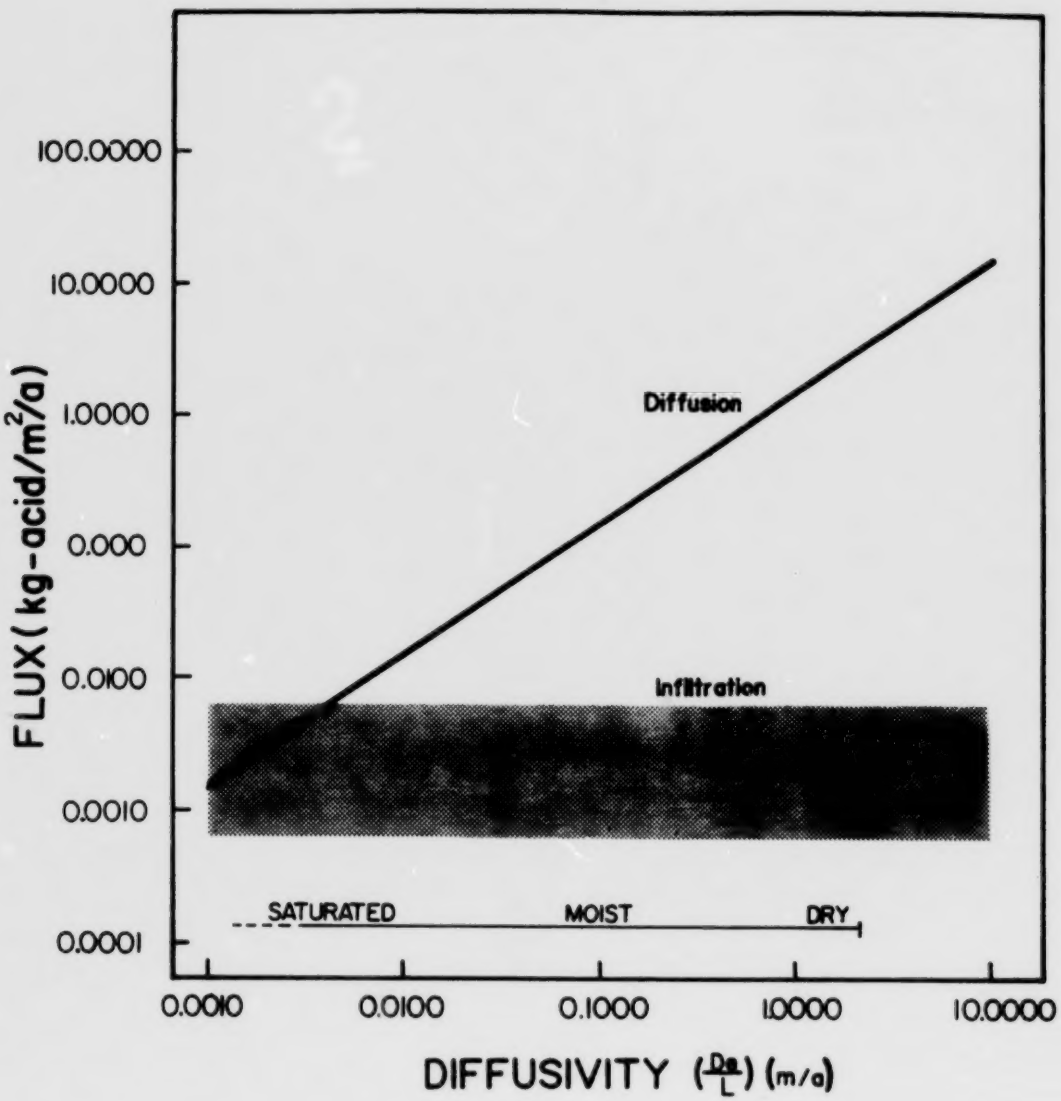


FIGURE 2.13: OXYGEN FLUX EXPRESSED AS H_2SO_4 ACID PRODUCED AS A FUNCTION OF ANNUAL INFILTRATION AND THE EFFECTIVE DIFFUSIVITY OF THE COVER

a^{-1}. The value of L will not likely be more than about 2 m, and will probably be close to 1 m for practical purposes. Therefore, the range of values for D_e/L are close to the range of values for D_e alone.

The relationship between the diffusive flux and the mass transfer term is shown graphically in Figure 2.13. In this figure, the flux of oxygen has been converted to the equivalent flux of acid that would be produced by reaction of the oxygen with pyrite. This acid flux represents a total available acidity (as H_2SO_4) that would be produced, and is based on the stoichiometric relationship between oxygen and pyrite in the production of acid. This figure shows that the maximum flux of oxygen is equivalent to about 10 kg of H_2SO_4 per m^2 of tailings per year, when oxygen diffuses through a very dry cover material. When the material has a greater moisture content, and diffusion is the controlling process, values are considerably reduced. The resulting flux can be as low as 1 g or less of H_2SO_4 per m^2 per year. However, on the same diagram, it can be seen that the advective flux of oxygen occurs within the range of about 1 to 10 g of H_2SO_4 per m^2 per year. Because the infiltration rate is independent of diffusion, the flux of dissolved oxygen will represent the minimum limit for oxygen transport through the cover.

This lower limit to oxygen flux is not practically affected by low permeability cover materials. The lower limit considers an infiltration rate of about 0.01 m a^{-1}, which is equivalent to the flow under unit gradient through a material having a hydraulic conductivity of about 3×10^{-10} m s^{-1}. This value would be typical of a clay till or marine clay (Freeze and Cherry, 1979), and it would be difficult to reproduce this property under field conditions. Therefore, the lower limit for the flux of dissolved oxygen will depend on the net infiltration rate and, therefore, will not likely be much lower than that shown in Figure 2.13.

The natural infiltration rate may be reduced through use of multilayered cover systems which would include drain layers and appropriate grading. Single layer covers would not likely exhibit hydraulic conductivity values that are less than 10^{-10} m s^{-1}.

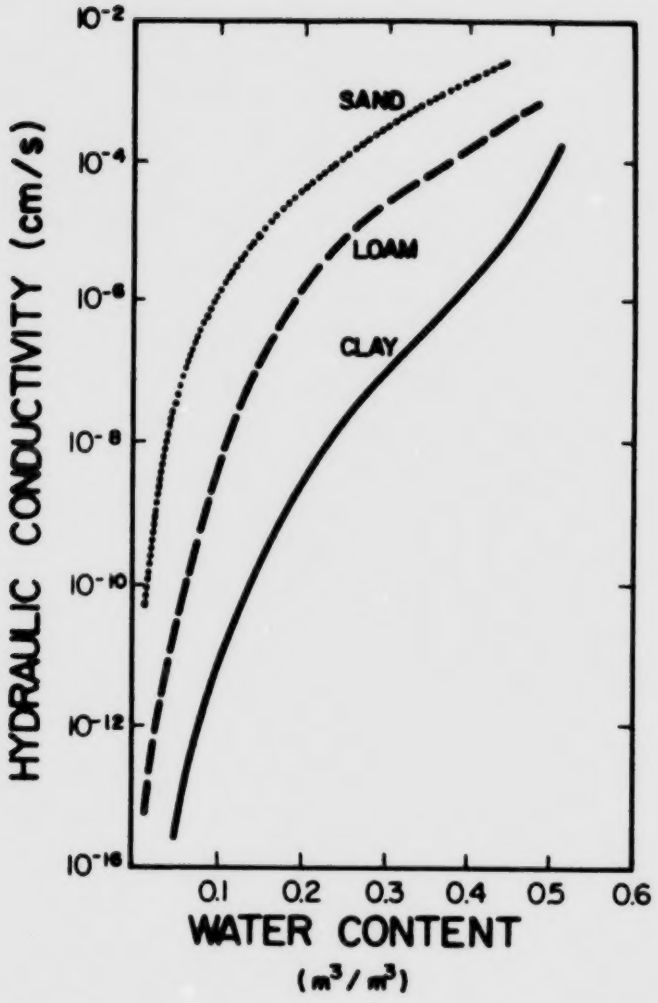


FIGURE 3.1: HYDRAULIC CONDUCTIVITY AS A FUNCTION OF WATER CONTENT

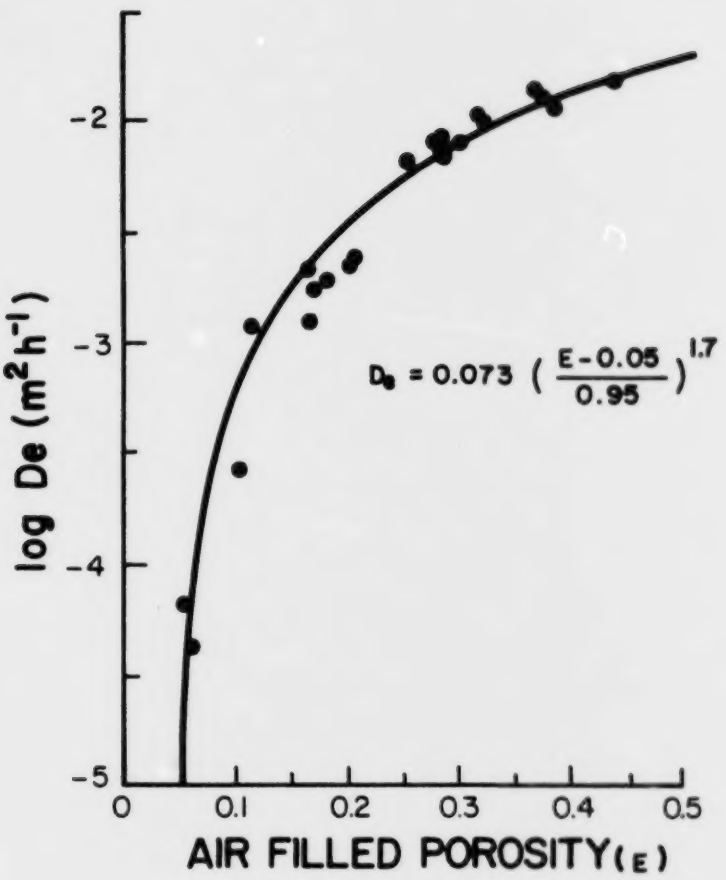


FIGURE 3.2: EFFECTIVE DIFFUSION COEFFICIENT AS A FUNCTION OF AIR-FILLED POROSITY FOR A SAMPLE OF ELLIOT LAKE URANIUM TAILINGS (after Reardon and Moddle, 1985)

3.0 CRITICAL PARAMETERS

3.1 Parameter Interaction

Some of the functional relationships between important parameters have been shown in previous sections. The purpose of this section is to summarize the interaction between these important parameters, and provide graphical representation of these relationships.

The water content within the tailings cover will be related to the pressure head distribution and grain size distribution characteristics for a specified cover material. When the water table is relatively shallow, the pressure head will represent the distance between a specified elevation in the cover and the water table. The typical relationship between water content and pressure head has been shown in Figures 2.2 and 2.3. This relationship can be determined in the laboratory for a specified material. The relationship is hysteretic such that different values of moisture content are obtained at the same pressure head value depending on whether the material is going through a wetting or a drying cycle. Hysteresis does not affect the upper end of the curve where the medium is saturated under low to moderate pressure head values. In any cover layer design, therefore, it would be desirable to use as fine grained a material as possible to provide a large range of pressure heads for which the material remains saturated or near saturated.

The hydraulic conductivity of a medium is also a function of the water content as discussed in Section 2.2.1. This relationship is shown graphically in Figure 3.1. This relationship is not hysteretic.

The effective diffusion coefficient for oxygen in a cover layer can be shown to be a function of the water content. This relationship is shown graphically for a sample of tailings from Elliot Lake in Figure 3.2. It is evident that the value of D_e is quite sensitive to the moisture content (and therefore air-filled porosity), especially when the medium approaches saturation. The relationship between D_e and the air-filled porosity is given by the following empirical equation (Troeh, et al, 1982):

$$D = ((E-a)/(1-a))^b \qquad (3.1)$$

in which a and b are experimental coefficients. It is necessary to determine the value of these cofficients for porous media with different textures.

3.2 Selection of Critical Parameters

The overall selection of critical parameters should ideally identify a small number of controlling variables. Key parameters that control the system overall, and those that can be related directly to field and/or laboratory measurements, are desirable.

The key parameters of interest for oxygen transport through a tailings cover are; the volumetric water content (w) the soil water pressure head (p_w), the effective gas diffusion coefficient (D_e), and the saturated hydraulic conductivity (k_s). Of these, the volumetric water content is the least difficult to measure. The three other parameters are a function of water content.

The interdependence of the water content and pressure head is expressed by the soil water characteristic curve (see Section 2.2.1 and Figure 2.3). Each tailings cover material will have a unique soil water characteristic curve. The water content and associated pressure head can be measured in the field, and monitored and controlled in the laboratory. Selection of an appropriate cover material will be based on the ability of the material to withstand significant negative pressure head values while remaining at or near saturation (i.e., near or above the air entry value). Because the ideal cover should remain near saturation to reduce diffusion of oxygen, the water content at a number of selected pressure head values should be used as criteria for ranking proposed cover materials.

The hysteretic nature of the water content versus pressure head relationship introduces a measurable degree of uncertainty in the prediction of one of these parameters when the other is known. However, this may not be of concern if the pressure head remains near the air entry value for the particular cover material. Even when conditions are such that hysteresis is significant, it is possible to predict water content with more sophisticated modelling efforts, and/or detailed monitoring of the wetting and drying history of the material.

Water content is also known to be the key parameter controlling the effective gas diffusion coefficient. Because the gas diffuses primarily through continuous gas-filled pores, higher water content results in lower effective gas diffusion coefficients (see Section A8, Part 3). The effective diffusivity of the cover can be predicted from known values of water content after experimentally obtaining the two parameters that are related to grain size and texture of the specific material.

The saturated hydraulic conductivity is a critical parameter for the control of water movement (with dissolved oxygen) through potential cover materials. However, it is of lesser importance than the three parameters listed above for two important reasons. First, the mass of oxygen transported in dissolved form in water is usually small relative to that which would diffuse through the cover if it were dry. Second, only soils with large percentages of clay can significantly impede natural infiltration. If clay soils are disregarded for practical reasons, such as lack of availability, then it is fair to assume that most of the natural rainfall and snowmelt, less natural evapotranspiration, will infiltrate the cover material. Evapotranspiration is an independent parameter not easily controlled, and will be the only process likely to limit the net water flux through the cover.

4.0 EVALUATION OF TECHNIQUES FOR MEASURING CRITICAL PARAMETERS

4.1 Selected Methods

4.1.1 Water Content (w) versus Pore-water Pressure Head (p_w)

The recommended technique for determination of the relationship between water content and pore-water pressure head (i.e., the soil-water characteristic curve) is the pressure cell apparatus (Klute, 1986). The pressure cell method is a standard technique performed in most soil physical properties laboratories. Klute (1986) provides a detailed discussion of the theory and procedures involved in the determination of the soil-water characteristic curve.

4.1.2 Relative Diffusion Coefficient versus Air-filled Porosity

Because the relationship between the relative diffusion coefficient and air-filled porosity is unique for a given soil, and exhibits great soil to soil variability, for each soil in question.

The method recommended is that of Reardon and Moddle (1986) (see Figure 4.1). In this method, a steady-state diffusion of CO_2 gas is established across a layer of soil. A constant concentration on the inlet side of a short soil column is maintained by continuous flushing of the head space with a specified gas mixture with a specified concentration of CO_2. The outlet end of the core is maintained at zero concentration of CO_2 by contact between the small volume of gas in the head space and a NaOH solution. The NaOH solution acts as a strong CO_2 sink. The flux of CO_2 can be calculated by continuously monitoring the electrical conductance of the NaOH solution, which increases in conductance in direct response to the amount of CO_2 that dissolves (see Reardon and Moddle (1986) for a more comprehensive discussion of the mechanisms involved). The use of CO_2 gas allows the relative diffusion coefficient of the porous medium to be calculated without need to consider sink and/or source terms for oxygen in the diffusion equation. Because the relative diffusion coefficient at a given water content is a physical constant and is independent of the gas used (Reardon and Moddle, 1986), the oxygen diffusion coefficient can be calculated from the CO_2 data.

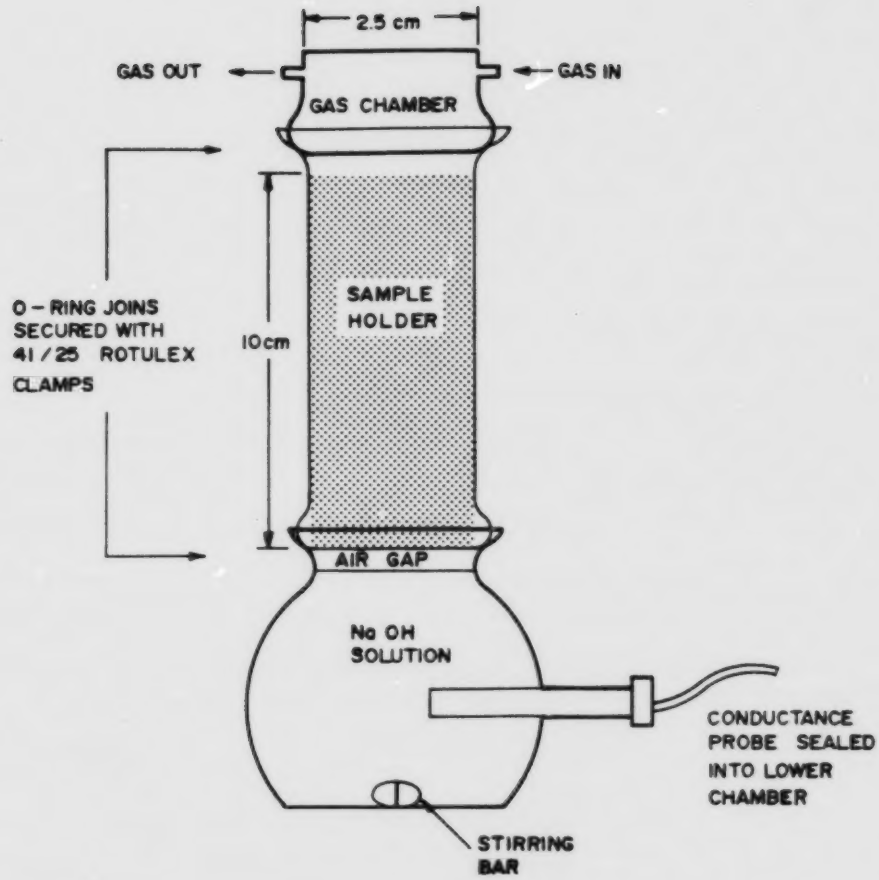


FIGURE 4.1: SCHEMATIC ILLUSTRATION OF REACTION CELL USED IN DIFFUSION COEFFICIENT MEASUREMENTS (after Reardon and Moddle, 1985)

The determination of the relative diffusion coefficient at a number of different air-filled porosities should be conducted and the data fitted using the equation presented by Troeh et al. (1982):

$$D = ((E-a)/(1-a))^b \qquad (4.1)$$

Packed columns of differing air-filled porosities (or water contents) should be prepared using one of the following two methods. For the high air-filled porosity range (low water content), air-dried soil samples should be throughly mixed in a sealed plastic bag with the required mass of water. The damp soil should then be carefully packed into the test columns.

For the low air-filled porosity (high water content) range, a pressure plate cell apparatus should be used. The apparatus that is commercially available will convert a soil sample or column into a single sample pressure cell apparatus which works in the 0 to -10 m of water pressure range. The soil column could be equilibrated to the desired air-filled porosity value. Then, by removing the porous plate end caps and replacing them with the diffusion apparatus end caps (see Figure 4.1), a gas diffusion experiment can be conducted.

4.2 Recommended Laboratory Approach

The purpose of a laboratory investigation should be to determine the rate of movement of oxygen through selected porous materials to verify the predicted diffusion of oxygen through material with a spatial variable diffusion coefficient. Candidate materials may include readily available glacial silt tills, desulphurized tailings or lake bottom sediments, for instance. The characteristics of the selected material should be determined according to the methods outlined above. This includes measurement of the moisture content and pressure head relationship, as well as the dependence of the effective diffusion coefficient on moisture content. Saturated hydraulic conductivity could also be measured, but this is not a high priority. A laboratory experiment should then be designed to determine the effectiveness of this material in reducing oxygen movement, and verify the model that describes oxygen diffusion through the test materials.

It is important to note that the recommended laboratory experiments are based on some techniques that are relatively innovative in the context proposed here. By nature, these procedures are oriented toward research objectives because standard methods for the required measurements are not available. As indicated above, some of the methods for measuring oxygen, by platinum microelectrodes for instance, have been applied in other investigations, but have not been used in the manner recommended here. There are also methods proposed for uptake of oxygen at an interface to simulate contact with a sulphidic tailings layer. These too are non-standard techniques and would require refinement during the initial phases of any testing that is conducted.

The laboratory methodology could include the use of soil columns of varying lengths. The columns would contain the selected test materials. These could vary in length from about 20 cm to about 1 m and, therefore, the moisture content would vary throughout the column as a function of the pressure head change. The pressure head at the bottom of each column could be controlled with the pressure plate apparatus to simulate the desired depths of the water table in each column. There would be no need to actually have a water table within the column, and the pressure plate device would allow simulation of a water table far below the actual bottom of the column. An oxygen sink would be required at the base of each column to simulate the consumption of oxygen that would occur below a cover layer in reactive tailings. The flux of oxygen through the column will be measured, and oxygen concentrations along the length of the column will also be monitored.

4.2.1 Column Design

A schematic diagram of a recommended design for a soil column apparatus can be seen in Figure 4.2. The column will be constructed from a Plexiglas$^{(R)}$ cylinder (approx. 10 cm diameter). The top and bottom plates should be removable and could be sealed to the cylinder by rubber o-rings and clamps connecting the plates. These columns could consist of modified Temp Pressure Cells that are commercially available. The top plate would contain a gas inlet port and a small headspace for the air supply above the soil sample. The bottom plate could consist of a porous plate that could be modified to allow contact between the soil sample and an oxygen sink below.

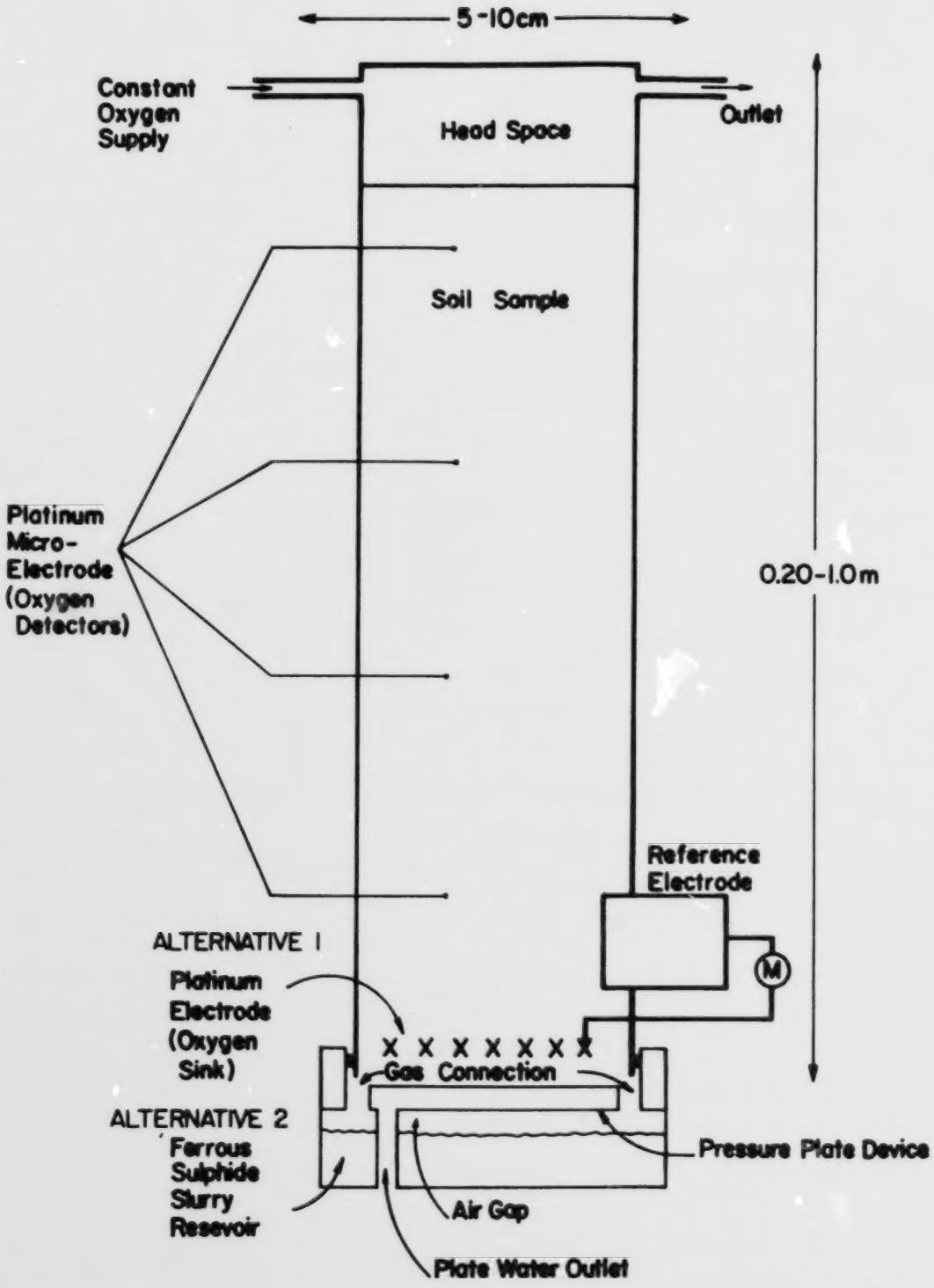


FIGURE 4.2: RECOMMENDED SCHEMATIC DESIGN FOR AN OXYGEN DIFFUSION CELL

A pressure plate consists of porous ceramic that transmits water but not air even when subjected to positive or negative pressures. The porous-plate material used should be impermeable to air up to about 1 atmosphere pressure or 10 m of pressure head. A selected gas pressure could be established within the column through the inlet on the top plate of the column. Because the bottom will be "open" only through the porous plate and because the porous plate is impermeable to air, the gas will not flow out of the column base. Water will be expelled until the water content of the soil attains equilibrium between the internal pore-gas pressure and the outside or atmospheric pressure. This is how the water content will be controlled in the column.

The depth of the water table below the bottom of the porous plate could be simulated by adjusting the gas pressure within the column. The value of the gas pressure within the pore spaces in the soil is equal to the negative pressure experienced by the moisture in those pores and the negative pressure is used to calculate the resulting "depth" of the water table. The water content will then be a function of the distance above the water table or pressure head in the soil pores. The precise relationship will have been determined previously during the testing of pressure head versus water content relationship.

An oxygen sink should be installed at the base of the column to simulate oxygen consumption that would occur if sulphidic tailings were in contact with the soil in the column. Two alternatives for an oxygen sink are recommended. One is based on oxygen consumption that would occur on a platinum electrode with a voltage applied between the platinum and a reference electrode located in the column. The second method involves a slurry containing reduced active FeS that readily consumes any oxygen that comes in contact with it. Details for these alternate methods are presented below.

4.2.2 Oxygen Sink Alternatives

The platinum electrode approach is based on the reduction of oxygen that occurs on the platinum when a voltage exists across the surface. The electrode could be designed as a mesh that would be installed within the soil immeditely above the pressure plate. A reference electrode could be inserted and sealed into the cylinder above the base plate to ensure contact with the soil. A precise and controllable voltage would be applied across the platinum and reference electrodes. Measured current would be used to calculate the flux of oxygen reduced on the electrode.

This method has not been applied in such a manner previously. Platinum electrodes, however, have been used to measure oxygen flux in soils. The method recommended here represents an extension of previous applications in that the platinum would provide oxygen uptake at the base of the soil. This oxygen uptake would represent the consumption that would occur in sulphidic tailings under such a soil cover.

The use of a chemical sink is proposed as an alternative to the platinum electrode method. The method would require that oxygen be consumed rapidly and completely from the adjacent gas space. Amorphous ferrous sulphide is an example of such a reducing agent which has been used to produce anaerobic cultures (Brock and O'Dea, 1977). This material has also been used successfully in column experiments to maintain anaerobic conditions (anoxic) in simulated groundwater flowing through the columns (D.R. Lee, pers. comm., 1980).

The chemical slurry would be located at the bottom of the column with gas phase connection to the pore spaces in the soil sample. The actual chemical slurry would be isolated from the soil sample by a small head space that would allow oxygen to migrate and be consumed in the chemical slurry without affecting the soil column itself. This would be accomplished by constructing the appropriate seals on the bottom pressure plate that would maintain a continuous aqueous phase contact between the pressure plate and the soils, but allow the gas to bypass the pressure plate and contact the chemical slurry.

The chemical oxygen sink is preferable to that of the platinum electrode, because it is simpler and less prone to errors that may occur in the electronics associated with the platinum electrode method. The major disadvantage of this method is not being able to readily measure oxygen flux into the slurry.

4.2.3 Flux Measurement

The oxygen flux through the soil material will be related to the oxygen gradient established through that material and the effective diffusion coefficient for oxygen in the soil. The oxygen gradient could be established by specifying laboratory conditions (i.e., atmospheric oxygen concentration at the surface and zero concentration at the base of the column sample). The flux of oxygen through the soil sample would then represent

the resulting oxygen diffusion occurring through the soil which would have a spatially variable water content. The flux is, therefore, an important measurement in this investigation. The measurement technique will depend on the type of oxygen sink used in the experiments.

If a platinum electrode is used as an oxygen sink at the base of the column, the oxygen flux would be measured by the electrode current. This method can be affected by instrument drift and possibly by electrode poisoning, but should yield reasonable results if oxygen is available at the electrode surface.

The use of a chemical oxygen sink at the base of the soil column will require development of alternative techniques to measure the flux of oxygen. It is probable that a reservoir of ferrous sulphide slurry could be sampled periodically to determine sulphate concentrations which result from oxidation of the sulphide component in the mixture. If the oxidation reaction were complete, then sulphate should be an excellent indicator of oxygen entering the slurry. This method of measuring oxygen flux would require investigation. Preliminary testing would be required to determine the rate of oxygen uptake when exposed to air and the accuracy and resolution of the method.

4.2.4 Oxygen Concentrations in the Column

An oxygen concentration gradient will be introduced across the soil sample during an experimental run. If the soil properties are homogeneous (i.e., constant diffusion coefficient), then the steady-state concentration gradient will be linear from the top to the base of the column. This means that oxygen concentrations measured through the column would exhibit a linear decrease with depth. Because the soil materials are not expected to be completely homogeneous, and because it is important to determine the more realistic behaviour of a thicker column of soil that may represent conditions in the field, the concentration gradient is not expected to be linear across the sample. This will also be the case because the water content may vary with depth through the soil sample. To gain a better understanding about this none ideal behaviour and to validate the mathematical models, it will be important to measure oxygen concentrations in the gas phase with depth in the soil column.

If the test material is expected to have some oxygen consumption potential, as would be the case with lake sediments for instance, these would be evaluated before an oxygen sink was introduced. The oxygen concentrations would be measured prior to introducing the oxygen sink at the base of the column. In this case, the appropriate model would include a sink term for the layer being tested.

It is recommended that oxygen concentrations be measured with microelectrodes (platinum) located at selected intervals along the column. The technique has been applied successfully in the laboratory and in the field for measurement of oxygen concentrations in soils. The concentration values would be used to validate the predictive model and to verify the diffusion coefficient value determined from the oxygen flux calculation.

4.2.5 Data Collection

After preparing the soil column by packing the appropriate soil and adjusting the water content, an air supply with a known oxygen content should be passed through the head space at the top of the column. The oxygen flux and oxygen concentrations at specified intervals through the column will be measured with time. The flux and oxygen concentrations should attain steady-state values after a period which will depend on the effective diffusion coefficient of the material being tested. The data should be collected until steady-state is attained.

The bulk water content for the sample should be obtained by weighing the column before and verifying the weight after the experimental run. The moisture content profile could be obtained from a small diameter core of the soil column extracted at the completion of the experimental run. The core should be segmented and moisture content measured on each of the segments.

4.2.6 Data Evaluation

The bulk diffusion coefficient for the soil in the column should be calculated from the oxygen flux measurements and the known oxygen concentration gradient and length of the column. The detailed analysis is more critical, however, and will involve modelling of oxygen concentrations at the selected intervals through the column that result from

the water content profile that controls oxygen diffusion through the soil. Each material should be tested under variable conditions of moisture content that results from different pressure head values within the soil column (i.e., simulated height above the water table). Different lengths of columns varying between 0.1 and 1.0 m could be used in the experiments to determine whether or not non-ideal effects occur over these intervals.

5.0 RECOMMENDATIONS

This report outlines a recommended methodology for assessing the effectiveness of various soils and fine-grained tailings as a cover in restricting the entry of oxygen into the tailings. The purpose of the cover is to reduce the rate of sulphide oxidation to acceptable levels so that the slightly affected pore water seepage could be neutralized by the natural buffering capacity of the tailings or underlying geologic deposits. The recommended laboratory method for determining the rate of movement of oxygen through these porous materials is based on innovative laboratory techniques which would require refinement during fabrication and testing of this laboratory apparatus. The proposed column design would have to be evaluated to:

- o select the oxygen sink alternative of the platinum electrode approach or ferrous sulphide slurry method;
- o test the platinum micro-electrode behaviour in the porous material;
- o test the ferrous sulphide sink method for kinetic effects;
- o evaluate the potential for measuring flux of oxygen at the base of the column with either the platinum electrode or ferrous sulphide sink method.

The next step would be to demonstrate and standardize the procedure using reference material for calibration. Once this is completed, a reactive tailings site should be selected and assessed for existing fine-grained porous materials in close proximity to the site. This may include such porous materials as fine-grained silts or inert tailings. These materials will then be assessed in the laboratory for their effectiveness in limiting oxygen movement into the tailings.

Model development will be required to assess oxygen diffusion for the soil under different pressure heads to simulate height above the watertable which results in variable moisture content. Modelling is also required for selection of a cover which may consist of a composite of porous materials, possibly with alternate thicknesses, resulting in a need to assess the composite diffusion coefficient and hydraulic conductivity. The newly developed laboratory methods could be used to assess composite cover designs and to calibrate the model.

Finally, laboratory testing of cover materials could be conducted with actual tailings samples. These tests could be designed to measure the effectiveness of the materials

evaluated previously. A modified computer-based model would be used, and the predictions validated with the experimental results. This would represent the final validation needed before initiating field trials.

After evaluating cover designs based on the laboratory tests, field trials would be warranted to test the performance of the preferred cover materials and cover design in limiting oxygen movement into the tailings mass. The performance evaluation for the field trials will likely require development of monitoring systems to test the performance of the field trial.

The documentation of laboratory and field techniques will provide a methodology for conducting and interpreting the test results which will provide an engineering design basis for soil covers.

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APPENDIX 1

Terms of Reference

Centre de Recherches Noranda
240 boulevard Hymus
Pointe-Claire, Quebec H9R 1G5
Tél. (514) 697-6640
Télex 05-822647

noranda

4 December 1986

Mr. Don Fraser
Science Procurement Officer
Science Branch
11C1, Place du Portage, Phase III
11 Laurier St.
Hull, Quebec
K1A 0S5

SUBJECT: DEVELOPMENT OF LABORATORY METHODOLOGY FOR EVALUATING EFFECTIVENESS OF ENGINEERED COVERS FOR REACTIVE TAILINGS - DSS File 15SQ.23317-6-1736

In response to your request dated 21 November 1986, attached is a proposal to develop a laboratory methodology to evaluate alternative material covers for reactive tailings.

Our proposal has modified your statement of work to reflect the need for ensuring a proper development of laboratory equipment and methodology prior to assessment of various solid cover materials. This change was discussed with, and agreed to by, R. John, Manager NUTP program.

Total cost for this proposal is $28,000, and execution will require 3 1/2 months (mid-December 1986 to 31 March 1987). Part of the work will be subcontracted.

In view of the tight schedule to complete this work, your early authorization to proceed would be appreciated. Please contact K.G. Wheeland or R.S. Siwik if there are any questions, or if additional information is required.

Yours truly,

CENTRE DE RECHERCHE NORANDA

J. Mantel for PT

P. Tarassoff
Director of Research and Development

bc: F. Frantisak/H. Veldhuizen
P. Tarassoff/G.R. Kubanek/
L. Dagenais
JN/SP/File N-8635
R.S. Siwik
K. Wheeland

PT/vs

Encl.

CENTRE DE RECHERCHE NORANDA

PROPOSAL TO DEPARTMENT OF SUPPLIES AND SERVICES CANADA

DEVELOPMENT OF LABORATORY METHODOLOGY FOR EVALUATING EFFECTIVENESS OF ENGINEERED COVERS FOR REACTIVE TAILINGS

DSS File 15SQ.23317-6-1736

Prepared by : R.S. Siwik, Environmental Research Engineer
K.G. Wheeland, Head, Environmental Technology

Authorized by : P. Tarassoff
Director of Research and Development

Contact : R.S. Siwik or K.G. Wheeland

4 December 1986

Noranda Inc.
Centre de Recherche Noranda
240 Boulevard Hymus
Pointe Claire, Quebec
H9R 1G5
(514) 697-6640
Telex: 05 822647
Telecopier: (514) 697-7304

SUMMARY

This proposal outlines the development of a practical laboratory methodology for predicting the effectiveness of alternative cover designs in controlling the rate of oxygen and water movement into reactive tailings.

The scope of work consists of a critical review of the state of art and definition of suitable equipment and methodologies to conduct laboratory measurements of oxygen diffusion rates and hydraulic conductivity of non-synthetic solid cover materials such as clay, silts, slag, and silicious tailings. Part of the work will be subcontracted.

(Subsequent necessary steps, not included in this scope of work, would include fabrication of the equipment, demonstration of the methodology, and comparison of laboratory and field results for a series of materials.)

The total cost of this proposal is $28,000, and the work will required 3 1/2 months (mid December 1986 to 31 March 1987).

1. INTRODUCTION

1.1 Background

A major concern of both the National Uranium Tailings Program (NUTP) and the Reactive Tailings Program (RATS) is the prevention of oxidation of reactive (acid-generating) sulphide tailings and wasterock, and consequent release of acidic, metal-contaminated water to the environment.

One of the most important factors controlling the rate of oxidation of sulphide minerals in tailings is the availability of oxygen. One proposed method of reduction of sulphide oxidation is the application of engineered covers over reactive tailings. An engineered solid cover would minimize the rate of water and oxygen movement into tailings, therefore reducing oxidation of sulphide minerals and resulting in a trivial level of seepage.

A reliable laboratory-scale methodology to predict the effectiveness of alternative solid covers in preventing the diffusion of oxygen and penetration of water to the tailings would be an essential tool in designing an engineered solid cover for a reactive tailings disposal area on reactive waste rock dumps.

In discussion with R. John, Manager NUTP program, 3 December 1986, it was agreed that the scope of work should be initially limited to the development of the laboratory methodology.

1.2 Objective

Develop a laboratory methodology to evaluate the effectiveness of alternative solid cover designs in reducing the movement of water and oxygen to the underlying reactive tailings.

2. TECHNICAL PROPOSAL

2.1 Approach

The design of an engineered cover will be governed by the site availability of prospective site materials which could be sand, silts, inert tailings, etc. Evaluation of the potential cover materials should be investigated in the laboratory to assess their effectiveness in reducing air and water penetration. A laboratory methodology will be required to assess important parameters such as an oxygen diffusion coefficient, permeability, moisture content, oxygen consuming capability of the cover material, etc. indicating which of the available materials will be the most effective cover material and required depth.

2.2 Task 1 - Project Organization

This project will be undertaken by Centre de Recherche Noranda with the assistance of Beak Consultants and the Groundwater Institute at the University of Waterloo. The tentative project team is detailed in Section 3 and will be finalized upon project approval.

2.3 Task 2 - Data Review

A critical state of the art review will be conducted into existing techniques to assess oxygen diffusion and water movement in a porous media. It is intended to draw on work conducted in the NUTP program, and ongoing work at universities as well as in the hazardous waste industry.

2.4 Task 3 - Define Critical Parameters

Based on review of the theory of gas and water movement through a porous media and existing techniques, a list of critical parameters will be developed for equipment design.

2.5 Task 4 - Laboratory Design and Methodology

A preliminary laboratory equipment design will be provided indicating the approximate configuration and monitoring ports and apparatus.

2.6 Task 5 - Design Criteria

A methodology for conducting and interpreting the tests, to provide an engineering design basis for covers will be developed.

2.7 Task 6 - Reporting

Upon completion of the above tasks, a draft report will be issued for the review by the scientific authority. A final report will then be issued. As part of the final report recommendations will be made regarding further work required such as:

- fabricate and demonstrate the facilities and methodology;
- evaluate a series of alternative cover materials;
- conduct comparison test of laboratory and field methods;
- document the engineering methodologies.

3. PROJECT MANAGEMENT

3.1 Centre de Recherche Noranda Personnel

The project manager will be R.S. Siwik. K. Wheeland and S. Payant will also participate. Curriculum Vitae are appended.

3.2 Sub-Contractors

It is anticipated that Beak Consultants (R. Nicholson) and University of Waterloo (R.R. Gillham) will assist in the state of art review and definition of the laboratory methodology.

3.3 Reports and Invoices

Monthly reports and invoices will be submitted to DSS and the Scientific Authority.

A final draft report will be submitted by 31 March 1987.

4. PRICE PROPOSAL

The cost of this proposal will be $28,000 as summarized in Table I. The major schedule and expected cash flow will be as per the attached DSS contract plan and report form.

TABLE I

COST ESTIMATE

NR Labour	Sub-Contract Labour	Material/ Equipment	Travel	Total
$10,500	$12,000	$3,000	$2,500	$28,000

NOTES:

1. Materials/equipment include literature aqcuisition and printing costs.
2. Travel includes two meetings with sub-contractors (Toronto) and meeting with Scientific Authority (Ottawa).
3. Subcontractor price subject to negotiation and workload.

5.1 Labour

Billing rates for Centre de Recherche Noranda personnel will be in accordance with the following negotiated rate:

$$\text{Hourly Rate} = \frac{\$ \text{ annual} + 155\% \text{ overhead}}{1885 \text{ hours}}$$

5.2 Equipment, Materials, Shipping and Disbursement

All items will be billed at cost with no markup.

5.3 Travel and Liaison

Costs will be in accordance with Centre de Recherche Noranda and DSS guidelines, billed with no markup.

5.4 Certification

We hereby certify that the labour rates quoted are based on costs computed in accordance with Contract Cost Principles DSS 1031-1, a copy of which we acknowledge to have received, and that the said labour rates do not contain an element of profit in excess of 0% of such costs.

Supply and Services Canada / Approvisionnements et Services Canada

CONTRACT PLAN AND REPORT FORM – FORMULE DE PROJET DE CONTRAT ET DE RAPPORT

CONTRACT TITLE – TITRE DU CONTRAT: Development of Laboratory Methodology for Evaluating Effectiveness of Alternative Eng. Covers

CONTRACTOR – ENTREPRENEUR: Centre de Recherche Noranda

ISSQ.23317-6-1736

TASK DESCRIPTION / DESCRIPTION DE LA TÂCHE	TASK DURATION IN MONTHS – DURÉE DE LA TÂCHE EN MOIS												TASK COST – COÛT DE LA TÂCHE		
	1 Dec.	2 Jan.	3 Feb.	4 Mar.	5	6	7	8	9	10	11	12			
1. Project Organiz.	———												1.0		
2. Data Review	———	———											12.0		
3. Parameter Eval.		———	———										2.0		
4. Lab Design Criteria		———	———										4.0		
5. Design Criteria		———	———										5.0		
6. Reporting	———	———	———	———									4.0		
PLANNED COST BY MONTH – COÛT PRÉVU POUR CHAQUE MOIS	2.0	10.0	10.0	6.0									PLAN 28.0		
ACT. PÉRIOD. / E.T.C. BY MONTH – PRÉVISION POUR CH. MOIS														ACTUAL – COÛT RÉALISÉ	E.T.C. – À VENIR

APPENDIX

CURICULUM VITAE FOR:

- R.S. Siwik
- K.G. Wheeland
- S. Payant

CENTRE DE RECHERCHE NORANDA

CURRICULUM VITAE

Name: Richard S. Siwik, P. Eng. (N.B.)

Position: Environmental Research Engineer

Department: Environmental Technology

Education:
. B.Sc. in Civil Engineering
University of New Brunswick, 1979

. M.Sc. (Civil/Environmental Engineering)
University of New Brunswick (in progress)
Thesis on Application of Water Quality Model
on a New Brunswick River

Associations:
Canadian Land Reclamation Association
Canadian Society of Civil Engineering
American Society of Surface Mining and Reclamation
Association of Professional Engineers of N.B.

EXPERTISE and EXPERIENCE

General

- Reclamation of reactive and non-reactive tailings.
- Mine-mill water management and effluent treatment plant optimization.

Specific

- Undertaking hydrogeochemical investigation of sulphide tailings dam.
- Developing reclamation closure plans for sulphide mine-mill sites.
- Evaluating bactericides for control of acid generation.
- Assessing wind erosion control techniques on sulphide tailings.
- Assessing storage stability of mine mill waste products.
- Process design for effluent treatment plants.

ADDITIONAL COMMENTS

- Previous experience includes water management and tailings disposal and reclamation projects for the Horne Division.
- Presentations on tailings management.

CENTRE DE RECHERCHE NORANDA

CURRICULUM VITAE

Name: Kenneth G. Wheeland, Eng.

Position: Department Head

Department: Environmental Technology

Education:
- B.A.Sc in Chemical Engineering, University of Toronto, 1956.
- Post graduate courses in Business Administration; Management by Objectives, Problem Solving.

Associations: Order of Engineers of Quebec; Canadian Institute of Mining and Metallurgy; Human Factors Association of Canada; American Industrial Hygiene Association; Canadian Pulp and Paper Association

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EXPERTISE and EXPERIENCE

- Experience includes process development, plant design and environmental control responsibilities in the oil refinery, intermediate chemical, aluminum, mining and forest product industries.
- Responsible for all department activities related to effluent and solid waste control, ecological evaluations, industrial hygiene and ventilation projects, noise abatement, process control.
- Active on ad hoc co-operative technical committees with other companies and government agencies re tailings management, industrial hygiene technology development and similar topics.

ADDITIONAL COMMENTS

- Several presentations and publications related to impact assessments, noise abatement, effluent treatment and emission control.

CENTRE DE RECHERCHE NORANDA

CURRICULUM VITAE

Name: Serge Payant

Position: Environmental Control Technologist

Department: Environmental Technology

Education: DEC (Analytical Chemistry), CEGEP, Valleyfield, 1975.

EXPERTISE and EXPERIENCE

- Experienced in instrumental and wet chemical analytical techniques (8 years).

- Bench and field evaluations of cyanide destruction, lime treatment, thiosalt destruction.

- Experimental studies regarding stability of sludges, leachability of tailings and other solids, control of acid generation by high sulphide tailings and wasterock.

APPENDIX 2

Fundamental Soil Properties
Static Mass and Volume Relationships

APPENDIX 2: FUNDAMENTAL SOIL PROPERTIES - STATIC MASS AND VOLUME RELATIONSHIPS

An unsaturated soil can be viewed as a three-phase system comprised of solid particles packed into a framework with the spaces between the particles filled with liquid water and air (see Figure A1).

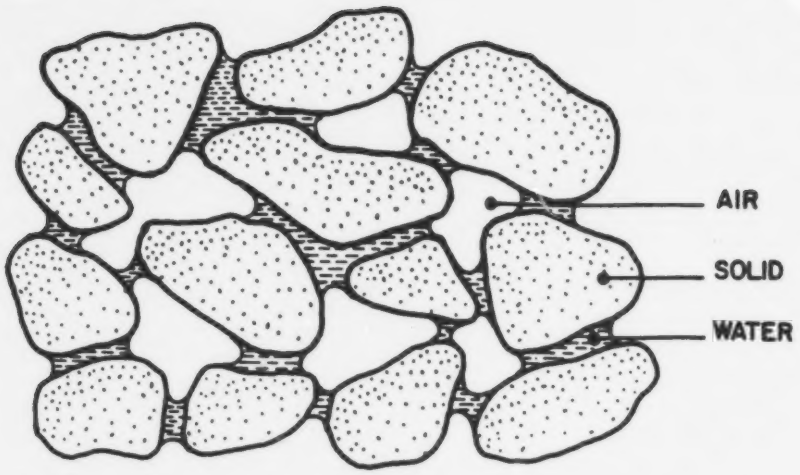
Texture refers to the particle size distribution of the soil. Figure A2 shows the textural triangle used to classify soils. For example, a soil that was made up of one-third clay size particles, one-third silt size particles and one-third sand size particles by weight would be called a clay loam. This property is important because the particle size distribution directly dictates the pore size distribution in structureless porous media.

Dry Bulk Density is defined as the mass of solid soil particles in a unit volume of bulk soil. This is usually determined by measuring the mass of a known volume of oven-dried soil (105°C until constant weight). The normal range of dry bulk density for reworked natural material, such as tailing covers, would be 1.1 to 1.6 kg/dm^3. The bulk density is also a measure of the degree of compaction. The higher the bulk density of a given material, the lower its porosity.

$$\text{Dry Bulk Density } (\rho_d) = \frac{\text{Mass of Solids } (m_s)}{\text{Total Volume of Soil } (V_T)}$$

Porosity is defined as the fraction of void space in a unit volume of bulk soil. This is determined by the difference in weight of the water saturated and oven dry mass of a soil sample (the mass of water being converted to a volume using the density of water of 1 kg/dm^3). Alternatively, the porosity can be calculated from the Dry Bulk Density and using a mean particle density based on the mineralogy of soil (2.65 kg/dm^3 for soils with less than 90% clay). The porosity of tailings cover materials would usually be between 0.3 and 0.6, depending on the soil texture and degree of compaction.

$$\text{Porosity } (n) = \frac{\text{Volume of the Voids } (V_v)}{\text{Total Volume of Soil } (V_T)}$$



Water in an unsaturated coarse-textured soil

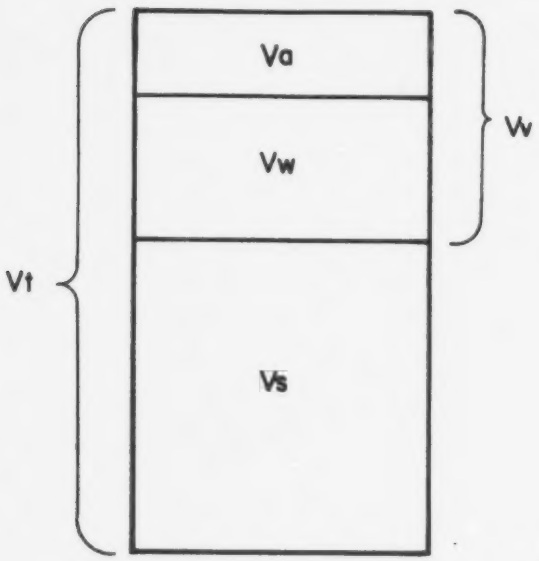


Figure A-1 - The Relationship of the Three Phases in a Soil; Volume of Air (Va); Volume of Water (Vw); Volume of Voids (Vv); Volume of Solids (Vs); Total Volume (Vt)

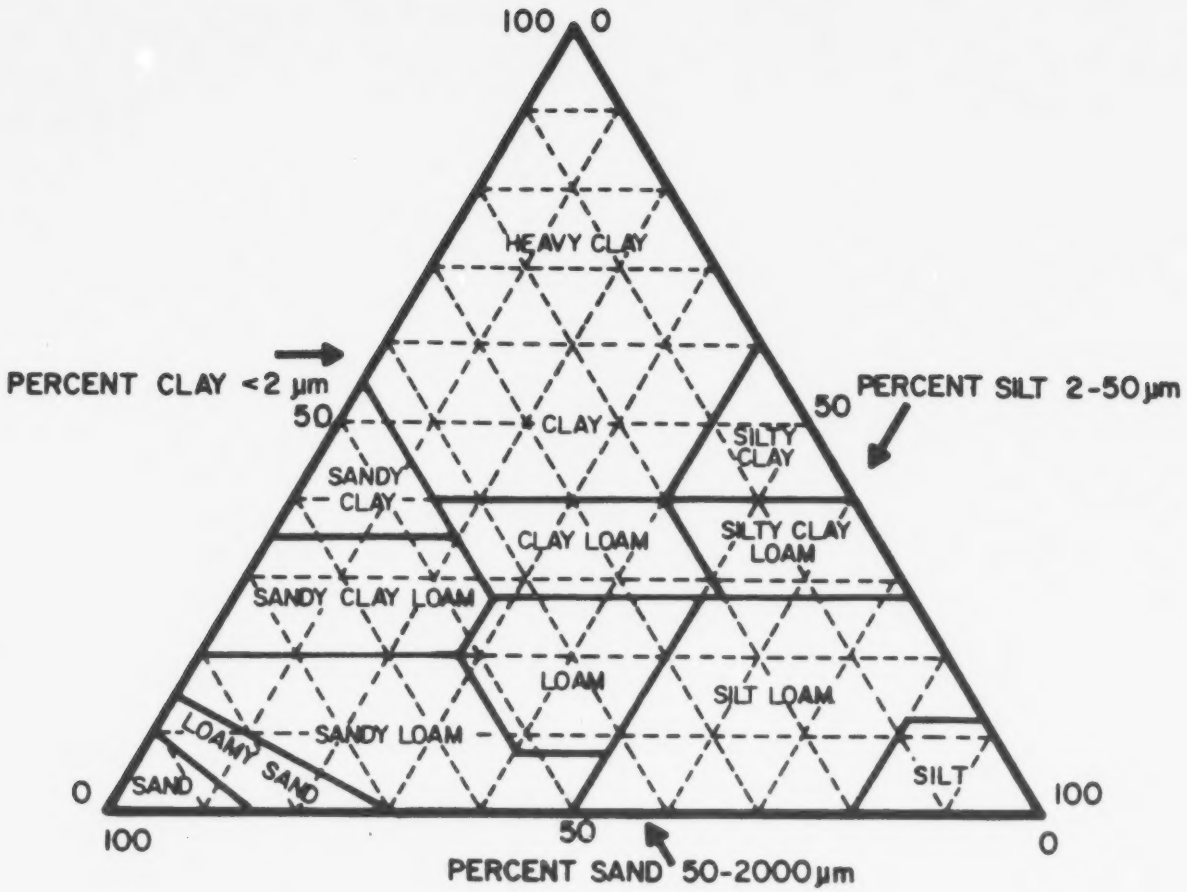


Figure A-2 - The Textural Triangle

or

$$\text{Porosity (n)} = 1 - \frac{\text{Dry Bulk Density of the Soil } (\rho_d)}{\text{Mean Particle Density } (\rho_s)}$$

Void Ratio is often used in the engineering literature in place of porosity. The void ratio is defined as the volume of the voids divided by the volume of the solids:

$$\text{Void Ratio (e)} = \frac{\text{Volume of the Voids } (V_v)}{\text{Volume of the Solids } (V_s)}$$

Void Ratio can be converted to porosity using:

$$\text{Porosity (n)} = \frac{\text{Void Ratio (e)}}{(1 + \text{Void Ratio (e)})}$$

Soil Wetness can be expressed in a number of commonly used ways:

1. The degree of water saturation (S_w) is defined as the volume of water in the soil divided by the volume of void space. Clearly, the degree of saturation would have a range of 0 to 1 for oven dry to saturated soils respectively:

$$\text{Degree of Water Saturation } (S_w) = \frac{\text{Volume of Water in Soil } (V_w)}{\text{Volume of Void Space } (V_v)}$$

or

$$\text{Degree of Water Saturation } (S_w) = \frac{\text{Volumetric Water Content (w)}}{\text{Porosity (n)}}$$

2. Mass water content is defined as the mass of water in a given volume of soil divided by the mass of solids in that same volume. This is conveniently measured by weighing the soil sample wet and then reweighing it after it has been oven dried:

$$\text{Mass Water Content } (w_m) = \frac{\text{Mass of Water } (m_w)}{\text{Mass of Solids } (m_s)}$$

Mass water content can be converted to volumetric water content using:

$$\text{Volumetric Water Content } (w) = \frac{\text{Dry Bulk Density } (\rho_d)}{\text{Water Density } (\rho_w)} \times \text{Mass Water Content } (w_m)$$

Volumetric Water Content is defined as the volume of water in the soil divided by the total bulk volume of the soil. This is the more common way of expressing soil wetness. Volumetric water content varies from a value equal to the porosity to zero for saturated soils and oven-dried respectively:

$$\text{Volumetric Water Content } (w) = \frac{\text{Volume of Water in Soil } (V_w)}{\text{Total Volume of Soil } (V_T)}$$

Air Filled Porosity is analogous to volumetric water content, but is an expression of the volume of the gas phase (air) divided by the total soil volume. Air filled porosity ranges from a value of zero to a value equal to the porosity for saturated and oven dry soil respectively:

$$\text{Air Filled Porosity } (E) = \frac{\text{Volume of Air } (V_a)}{\text{Total Volume of Soil } (V_T)}$$

The sum of the volumetric water content and the air-filled porosity equals the total soil porosity.

$$\text{Air-filled Porosity } (E) + \text{Volumetric Water Content } (w) = \text{Porosity } (n)$$

The air-filled porosity is often quoted in studies of gaseous diffusion in porous media.

APPENDIX 3

LABORATORY METHODS FOR MEASUREMENT OF CRITICAL PARAMETERS

APPENDIX 3: LABORATORY METHODS FOR MEASUREMENT OF CRITICAL PARAMETERS

A3.1 Porosity

1. Gravimetric Techniques (Danielson and Sutherland, 1986)

a) Porosity may be determined from the mass of water in a saturated core. The saturated core is weighed and then oven-dried at 105°C until constant mass is obtained on a number of consecutive determinations. The mass of water is then converted to a volume of pores present in the known total sample volume, i.e., porosity.

b) Porosity may be determined from a bulk density (known mass of soil in a known volume) and a measured or estimated particle density. It is common to use a particle density of 2.65 g/cm^3 for soils with less than 90% clay content (Hillel, 1980, p. 10). Porosity is then calculated from one, minus the bulk density divided by the particle density (see Appendix A.1).

2. Air-Space-Pycnometer Method (Danielson and Sutherland, 1986)

a) A hanging water column and burrette are used to introduce a known volume change on a closed (sealed) sample volume. Using the imposed change in pressure and Boyle's Law (or the Ideal Gas Law), the gas-filled pore volume can be calculated. When conducted on an oven-dried sample, this method yields the porosity of the core. This was the method used by Brown (1970) in his study of oxygen diffusion barriers for controlling acid mine drainage.

A3.2 Volumetric Water Content

1. Gravimetric Techniques (Gardner, 1986)

a) The weight of the moist (partially saturated) sample is determined. The sample is then oven-dried and reweighed. The difference in mass is used to calculate the mass water content and/or the volumetric water content (see A.1).

b) A variation on (a) above is to dry the sample by successive saturations and burning off of alcohol. This procedure is much faster (1 hour vs. 1 day), but somewhat less precise due to the alcohol solubility of some soil fractions (such as organic matter).

c) When the dry bulk density of a sample of known volume is specified, then the water content can be calculated from a single sample mass determination. The mass in excess of that accountable by the bulk density is the mass of water in the sample.

2. Gamma or Neutron Attenuation (Gardner, 1986)

These techniques are based on the scattering of photons or neutrons by water molecules (primarily the hydrogen atoms). A source is placed on one side of a sample column and the detector on the other. After calibration for the oven dry bulk density of the soil, variations in the number of photons or neutrons reaching the detector is proportional to the water content. The advantage of this technique is that it is non-destructive and repeatable. However, the equipment is relatively expensive (Hillel, 1980a).

A.3 Air-filled Porosity (Danielson and Sutherland, 1986)

1. When the total porosity and volumetric water content is known, it is a simple matter to calculate the air-filled porosity as the difference between these two known values.

2. The air-space-pycnometer method described under the Porosity heading above can be used on partially saturated sample to determine air-filled porosity directly.

A.4 Pressure Head (or Hydraulic Head) in Unsaturated Porous Media(Cassel and Klute, 1986)

1. Tensiometers are commonly used to measure the negative pressure (tension) of soil water. Numerous designs are commercially available, all of which work on

the same principle. A porous cup, that will remain saturated over the range of soil tensions to be measured, is connected to a sealed water reservoir. The tension of the water in the reservoir is measured with a pressure gauge or transducer (see Hillel, 1980; Cassel and Klute, 1986 for a more thorough discussion). In practice, tensiometers are sensitive and relatively difficult to use if reliable reproducible data are required.

2. Thermocouple psychrometer method is an indirect technique of measuring soil tension. The relative humidity of the soil-air is measured and the soil-water tension is calculated. The method relies on the fact that the equilibrium water vapour potential of the ambient soil-air is equal to the soil-water potential. Dalton and Rawlins (1968) and Brown (1970) describe miniaturized thermocouple psychrometers that provide a high degree of precision (Hillel, 1980).

A.5 Soil Moisture Characteristic Curve (Volumetric Water Content vs. Soil Water Pressure)

1. Pressure Plate Apparatus (Richards, 1947; Klute, 1986)

This apparatus is commercially available and is capable of determining the w vs. $_{w}$ curve to very low pressure head (i.e., very dry soil, very large negative soil water pressure) of -150 m of water (-15 bars, -220 psi). For tailings covers investigations, this range of pressure head is seldom required. End caps that convert a soil column into low pressure range. Pressure Plate Apparatus are commercially available.

2. Tension Plate Apparatus (Klute, 1986)

This apparatus is also commercially available and is capable of determining the w vs. $_{w}$ over the pressure head range of 0 to -1 bar (-15 psi). Often this "wet end" of the curve is sufficient for cover design investigations. As discussed earlier, maintaining higher water contents is desirable in order to minimize the oxygen diffusion rate (Hillel, 1980a).

Once the soil moisture characteristic curve has been determined, it can be used to calculate pressure head from water content data, or visa versa, given due consideration for hysterisis.

A.6 Saturated Hydraulic Conductivity (Klute and Dirksen, 1986)

1. Constant Head Methods

A number of steady-state techniques can be used that represent the direct solution of Darcy's Law. A constant hydraulic head is maintained across the core and the volumetric discharge from the known cross-sectional area of the core is measured.

2. Falling Head Methods

Transient flow techniques are also used to determine saturated hydraulic conductivity because they are somewhat simpler and faster to conduct. However, the standard error of the mean is usually larger than for steady-state methods.

A.7 Unsaturated Hydraulic Conductivity

1. Direct Methods

Methods which measure the hydraulic conductivity of partially saturated porous media have been developd. However, these determinations tend to be very time-consuming (one month to get a single k value), and require special apparatus not readily available or commonly used (Moore, 1939; Childs, 1945; Richards and Moore, 1952; Croney et al., 1958; Corey, 1957; Nielson and Biggar, 1961; Elrick and Bouma, 1964; Klute and Dirksen, 1986).

2. Indirect Methods (Mualem, 1986)

Indirect methods are available for the calculation of the approximate unsaturated hydraulic conductivity from pressure head or volumetric water content. For example, Hillel (1980) lists the following empirical equations from Gardner (1980):

$$k(p_w) = -a/p_w^b$$
$$k(p_w) = a/(b-p_w^m)$$
$$k(p_w) = k_s/(1 + (p_w/p_w^*)^m)$$
$$k(w) = a\, w^m$$
$$k(w) = k_s\,(w/n)^m$$

where k is the unsaturated hydraulic conductivity, k_s is the saturated hydraulic conductivity, a, b and m are empirical constants, p_w is the soil water pressure head, w is the volumetric water content, n is the porosity and p_w^* is the soil water pressure head at $k = 1/2\ k_s$.

In addition, van Genuchten (1980) gives an empirical equation for prediction of the $k(p_w)$ relationship from saturated hydraulic conductivity and horizontal infiltration experiments.

A.8 Oxygen Diffusion Coefficients

1. Boundary Concentration Methods

These methods, both steady-state and transient, involve the monitoring of the change in oxygen concentration in a sealed chamber at one end of a soil core. The initial concentration in the chamber is less than or greater than the constant (atmospheric) oxygen concentration on the opposite end of the core. Various theoretical and empirical equations have been used along with minor variations and modifications in the basic apparatus design. However, this basic boundary concentration method has been used by Taylor (1949), Rust et al. (1957), Currie (1960), Gradwell (1961), McIntyre and Philip (1964), Shearer et al. (1966), Bakker and Hidding (1970), Pilot and Patrick (1971) and Rolston (1986), among others.

2. In Situ Probe Methods

a) Platinum Microelectrodes

Developed by Lemon and Erickson (1952), the platinum microelectrode works on the principle that, at low oxygen flux, the oxygen concentration at the platinum surface will be zero and the electric current will be proportional to the rate of oxygen consumption (diffusion to the probe). Phene (1986) gives a comprehensive review of the theory and use of the platinum microelectrode method.

Kowalik et al. (1979) used a platinum electrode inserted through neddle ports in a soil column to measure oxygen concentration profiles.

Phene et al. (1976) describe the use of a multiprobe automated system for measuring oxygen diffusion rates with depth in a soil profile.

b) Membrane Probes

Phene (1986) reviews the use of commercially available oxygen probes. Willey and Turner (1963) describe a robust precise in situ oxygen probe of the membrane type that is designed to provide continuous oxygen concentration values. While most membrane type probes have the drawback of requiring separate calibrations in air and water, Enoch and Falkerburg (1968) describe a double membrane modification to an oxygen probe that resulted in a single air/water calibration curve. The drawback was that the response time of the probe was increased.

c) Analytical - Gas Chromatograph

Lai et al. (1976) and Jellick and Schnabel (1986) use an inection method to calculate oxygen diffusion away from a point source. At time zero, a volume of oxygen is injected into the soil through a needle. At regular time intervals after the injection, very small samples are taken, through the same needle, and analyzed for oxygen concentration.

3. Indirect Method: Diffusion Coefficients from Air-filled Porosity

A number of theoretical and empirical relationships exist in the literature for calculating the effective diffusion coefficient. The following is a partial listing:

a) $D/D_o = 0.66\ E$ - Penman (1940); used by Brown (1970) in his study of mine spoil covers

b) $D/D_o = E^{3/2}$ - Marshall (1959) and the dry sand equation of Currie (1970) (in Sung-Ho et al., 1976)

c) $D/D_o = E^{7/6}$ - Millington and Quirke (1959)

d) $D/D_o = E^{5/3}$ - Sung-Ho (1976)

e) $D/D_o = E^{4/3}$ - Millington (1959) using previously published data

f) $D/D_o = (E^{10/3}/n^2)$ - Millington (1959) and recommended by Rolston (1986) in his review of the literature

g) $D/D_o = (E/_n)^4 (n)^{3/2}$ -wet sand equation of Currie (1970) (in Sung-Ho, 1976).

Where D is the measured diffusion coefficient, D_o is the diffusion coefficient of the same gas in free space, E is the air-filled porosity, and n is the total porosity. The ratio D/D_o is the relative diffusion coefficient. Troeh et al., (1982) gave the general equation

$$D/D_o = ((E-a)/(1-a))^b$$

where a and b are empirical constant. Troeh et al., (1982) provides an extensive table of values for u and v that fit a large percentage of data from the literature.

APPENDIX 4

Annotated Bibliography

APPENDIX 4: ANNOTATED BIBLIOGRAPHY

Armstrong and Beckett. (1985)

Extensive modelling of oxygen diffusion in plant roots is presented, along with the oxygen concentration in the water film around the root.

Bakker and Hidding. (1970)

A non-steady state method of determining the effective diffusion coefficient for oxygen into undisturbed soil cores is described. Calculations are made of the errors involved when neglecting the storage term, temperature and pressure variations, and the oxygen consumption and resistance in the ambient air. An extensive table reviewing the literature on the relation between air porosity and gas diffusion in soils is given.

Bornstein, Benoit, Scott, Hepler and Hedstrom. (1984)

Platinum electrodes and neutron moderation techniques were used to determine the oxygen diffusion rate (ODR) and soil-water content, respectively, in packed laboratory columns of silty clay loam. A linear relationship between ODR and soil-water content was observed for the wet range (16 to 47% water by volume). Graphs are presented that clearly show the relationship between ODR and soil-water content when water is applied to the column.

Brown. (1970)

A laboratory study, using a closed system, is used to assess the effectiveness of thin (a few inches) cover layers of non-reactive natural porous media for the reduction of oxygen consumption by reactive pyritic tailings. A steady-state finite difference model was used. It was concluded that Penman's (1940) equation ($D/D_o = 0.66E$) relating the relative diffusion coefficient to air-filled porosity cannot be used to estimate oxygen diffusivities of pyritic refuse. An air pycnometer was used to measure air-filled porosity. The amount of oxygen consumed was calculated from the change in pressure within the closed system. Occasional injection of nitrogen was used to offset pressure differentials within the chamber. The soil moisture characteristic curve was not mentioned.

Callebant, Gabriels, Minjnuw and deBoodt. (1982)

Laboratory columns of sandy loam and loamy sand were used. Gas sampling and platinum microelectrodes were used to determine oxygen concentrations and diffusion rates, while the soil-water pressure was monitored using mercury tensiometers. The relationship between depth to watertable and the monitored parameters was investigated, and showed an increase in oxygen diffusion with a deeper watertable.

Colvin. (1977)

Colvin cites Shumate (1971) (EPA Dast-42 14010 FRR 04/71) as saying that 10 to 15 feet of dry, granular soil would be needed to make a significant difference on the rate of oxygen transport through a cover. Used Taylor's (1949) transient diffusion method. Like most studies, the oxygen diffusion coefficient and oxygen uptake rate (i.e., reaction rate) are considered to be constant throughout the soil layer, but it is acknowledged that this may no in fact be a valid assumption. One, two and three layer cover designs are simulated using a steady-state mixing cell model.

Currie. (1960a)

A laboratory apparatus using a modified thermal conductivity gas analyzer and soil columns is described. Hydrogen gas diffusing into air is studied and the transient solution for a gas diffusing from a closed chamber into a porous soil column is given.

Currie. (1960b)

An equation based on theoretical considerations for porosity and the tortuosity of pores is given that equates the effective diffusion coefficient to gas filled porosity. A large variety of porous media is tested, including sand, talc, steel wool, ceramic beads, mica and salt, to name a few. An extensive table of empirical parameters for fitting a curve to the effective diffusion coefficient versus porosity data is given for the full range of materials tested.

Currie. (1961a)

The theory concerning oxygen diffusion into spherical soil aggregates in a soil is discussed and accompanying equations are given. The concept of a critical aggregate radius under which there is no anaerobic centre in the aggregate is introduced.

Currie. (1961b)

A non-steady state technique was used to investigate the relationship between gas (hydrogen) diffusion coefficients and air-filled porosity for a number of materials including glass beads, sintered glass, sand, carborundum, pumice and soil crumbs. The effect of inter- and intra-aggregate porosity is discussed. Numerous graphs of relative diffusion coefficients versus air-filled porosity are given. No single expression fits all data.

Enoch and Falkenflug. (1969)

Modification to the design of a Clark-type membrane-covered oxygen probe improved the probe so that only one calibration curve is needed for operation of the probe in air or water. The double membrane modification did increase the response time of the probe to five to eight minutes.

Grable and Siemer. (1968)

The diffusion of oxygen in soil was found to be determined primarily by air-filled porosity. Bulk density and aggregate size per se had little effect on the rate of diffusion or on the concentration of oxygen at rooting depth.

Gradwell. (1961)

A study of diffusion of oxygen through both packed and undisturbed soil cores. The transient method of Taylor (1949) was used as the basis of the analysis. The relationship between effective diffusivity and air-filled porosity was not found to fit the models in the literature (e.g., DeVries, 1950) for the undisturbed cores. This was attributed to soil structure, i.e., macropores. An attempt to experimentally quantify the oxygen sink term is presented.

Jaynes and Rogowski. (1983)

Fick's Law is compared with the Stefan-Maxwell equations for gas diffusion. It is concluded that the Fickian diffusion coefficient is not a constant. Rather, it is dependent on the diffusional fluxes of other gases and on the mole fraction of the gas in question. Examples of the cases when the Fickian gas diffusion coefficient can be considered constant are given as; the diffusion of a trace concentration of a gas through a gas mixture of any composition, equimolar counter-current diffusion in a binary gas mixture, and diffusion in a tertiary mixture where one gas is stagnant.

Jellick and Schnabel. (1986)

An in situ method, based on spherical diffusion of gas from an injection point is evaluated for the determination of diffusion coefficients of N_2O in field soils. A finite difference model was developed that incorporated initial conditions more consistent with the experimental data, than was possible using analytical solutions. The method involves the injection, through a needle, of a slug of gas at time zero, followed by periodic microsampling of the gas back through the needle. A linear relationship between relative gas diffusion coefficient and air-filled porosity is observed.

Kimball and Lemon. (1971)

A device that measured the rate of evaporation of liquid heptane from a porous steel plate buried in the soil is described. It is concluded that, at very shallow depths (top few cm), air turbulence and pressure fluctuation have a significant effect, but that soil aeration is mostly a diffusive process.

Kowalik, Barnes and Smiles. (1979)

Soil columns were equipped with small access ports through which small gas samples were drawn. The oxygen content in the gas was measured using an oxygen electrode. Using this set-up, a theory of oxygen diffusion in soil in which the rate of oxygen consumption varied with time was applied to describe the oxidation of a slurry of pig manure.

Lai, Tiedje and Erickson. (1976)

A method based on radial diffusion from a point source injection was used. A needle is inserted into the soil. Fifty ml of gas is injected and, at given time intervals, 0.25 mL samples are drawn back through the needle and analyzed using a gas chromatograph. The duration of each experiment was only four minutes; therefore, sink and source terms were considered negligible. A least squares fit of the theoretical solution is applied to the data to solve for the diffusion coefficient. A plot of effective diffusion coefficient versus air-filled porosity is given which fits the expression $D/D_o = E^{5/3}$.

Lemon and Erickson. (1952)

The original paper on the use of a platinum electrode to measure oxygen diffusion in soils. Data given show increasing oxygen diffusion rates with larger soil aggregates and greater soil porosity, along with decreasing oxygen diffusion rates with increasing depth in the soil profile.

Marshall. (1959)

Theory based on the bundle of capillary tubes model of flow through porous media is used to develop a non-linear expression for the relationship between the effective gas diffusion coefficient and air-filled porosity.

McIntyre. (1966)

The platinum microelectrode is stated to give reliable data only over the range of soil-water contents that maintain a water film on the electrode surface. This minimum water content, for which accurate oxygen flux rates could be measured with a 1.5 mm

platinum electrode, was achieved after two days of drainage from the saturated state for a well-drained soil. In a poorly drained soil, the platinum electrode was still operating after six days. A table of oxygen flux rate after one, two and three days of drainage, along with infiltration time for five inches of water, is given for a wide range of soil textures.

McIntyre. (1966)

The platinum microelectrode is tested on glass beads, a sandy loam and a loam. The dependence of current on the rate of oxygen flux to the electrode was found to be better for constant effective voltage relative to a reference electrode, rather than constant applied voltage.

Millington. (1959)

Theory is presented to support the relationship $D/D_o = E^{4/3}$, where D/D_o is the relative gas diffusion coefficient, and E is the air-filled porosity. The data of Taylor (1949), Penman (1940) and VanBave (1952) are compared to the theoretical curve. The agreement between theory and data is marginal.

Millington and Shearer. (1971)

Theory and an equation that relates the effective diffusion coefficient to the degree of saturation and the inter- and intra-aggregate water contents is given. A number of graphs of effective diffusivity versus air-filled porosity are given that compare the theory to experimental results for a number of aggregated soils and pumice. The agreement between the theory and experimental data is good.

Nielson, Rogers and Gee. (1984)

Theory is presented for calculating the diffusion coefficient of radon gas from soil-water content and pore size distribution data. Diffusion in both the air-filled and water-filled pores is considered. The model results compare well with measured values.

Papendick and Runkles. (1966)

The necessity of using a transient analysis because of non-constant oxygen consumption rates (sink terms) is discussed. A laboratory apparatus incorporating platinum oxygen electrodes, and a hanging water column (tension table) to maintain constant water contents is described. Plots of oxygen consumption rate versus time for a silty clay loam over the period of eight days is shown. An exponential decay in the oxygen consumption rate is observed.

Phene. (1986)

A detailed discussion of the theory and method of construction of platinum electrodes is presented, along with the design specifications and considerations for a basic oxygen diffusion rate measurement system. A fully automated field installation is discussed and a schematic diagram provided. In addition, the theory and application of the membrane electrode method is discussed with detailed schematics of probes and electronic curcuits.

Phene, Campbell and Doty. (1976)

A fully automated field system of measurement of oxygen diffusion rates (ODR) in a soil profile is described. Platinum microelectrodes are incorporated into the system design. The ODR at various depths in a sandy loam soil are monitored, and a distinct response to rainfall and irrigation events is shown.

Pilot and Patrick. (1972)

The method of Taylor (1949) was used to measure oxygen diffusion into soil with 200 ppm nitrate. A polarographic Clark type oxygen electrode was used in conjunction with a Beckman Model D oxygen analyzer. The redox potential of the soil was measured using 18-gauge platinum electrodes. At low air-filled porosities, no oxygen diffused all the way through the cores. At air-filled porosities above 11%, 12% and 14% for loamy sand, very fine sandy loam and silty clay loam respectively, oxygen diffused completely through the soil cores.

Pritchard and Currie. (1982)

A steady-state method in which the gas is injected at a steady but low rate into the end of a column is presented. Small (0.10 to 0.35 cm^3) samples are removed through sample ports in the wall of the column and then analyzed using a gas chromatograph. Tables comparing measured diffusion coefficients to those found in the literature are given.

Raney. (1949)

A robust <u>in situ</u> diffusion chamber is described for sampling gas in the unsaturated zone. A Beckman oxygen analyzer is incorporated into the design to determine oxygen diffusion coefficients. The effect of different tillage practices on diffusion rate is investigated.

Reardon and Moddle. (1986)

A steady-state method for meauring CO_2 diffusion in unsaturated pyritic tailings is presented. A sodium hydroxide solution is used as a sink for CO_2. The mass flux of CO_2 into the NaOH solution causes a change in electrical conductance. This change is used to measure the CO_2 discharge from the core. Oxygen diffusion coefficients are calculated using the CO_2 data and the fact that the relative diffusion coefficient (i.e., measured divided by the free space value) is independent of the gas used.

Rickman. (1968)

The effect of salts and soil solution electrical conductivity on platinum oxygen electrodes is discussed. The conditions under which a platinum electrode should work most satisfactorily or have minimum interference from salts are described.

Rogowski, Pionke and Broyan. (1977)

The lack of literature on spoil water flow, oxygen diffusion, surface runoff, erosion, evapotranspiration and temperature distributions within the spoil banks is pointed out.

Rolston. (1986a)

Recommended laboratory and field methods for the determination of gas diffusion coefficients of soils. The methods are transient and assume a non-reactive system, i.e., no source or sink terms.

Rolston. (1986b)

Three methods: (1) flux calculated from Ficks Law, (2) closed chamber method and (3) flow-through chamber method, are described for the quantification of the gas flux at and near the soil surface.

Rolston and Brown. (1977)

A laboratory column fitted with gas sampling ports is used to observe the diffusion of nitrogen gas into an Argon gas flushed air-dry loam soil. A field experiment is also described. A sealed chamber fitted to the soil surface is flushed with Argon. Nitrogen was then pumped through the chamber. The rate of flow and nitrogen concentration of the gas flowing out of the chamber through exit ports is used to calculate the flux of nitrogen into the soil. A plot of gas diffusion coefficient versus air-filled porosity is shown.

Rust, Klute and Gieseking. (1957)

A transient solution for diffusion from a closed reservoir into a soil core is given; however, no sink or source terms are included. The problem of mass counter flow caused by the differing diffusion coefficients of gases is discussed. To overcome the possibility of mass counter flow "self diffusion", using radioactive and non-radioactive carbon dioxide is used. A detailed schematic of the apparatus is given which incorporated the use of an air pycnometer for determining air-filled porosity.

Sallam, Jury and Letey. (1984)

A laboratory study was conducted to measure gas diffusion through soil at low air-filled porosities, using the inert gas Freon. Penman's (1949) model greatly overestimated, while the Millington-Quirk (1961) model slightly underestimated the diffusion coefficient. However, the Millington and Quirk model could be made to fit the data by using a slightly smaller exponent on the air-filled porosity term.

Shearer, Millington and Quirk. (1966)

An improved oxygen probe is presented along with a proposed laboratory apparatus for measuring oxygen diffusion through porous media. Design specifications are discussed and experimental results for capillary tube bundles are given. No sand data are presented.

Smiles and Griffin. (1966)

Methods of measuring oxygen diffusion in saturated porous media are examined relative to the platinum microelectrode technique. The effect of microbial respiration is discussed.

Taylor. (1949)

One of the earliest papers on oxygen diffusion in soils. This paper is frequently referenced as the source for equipment design when a closed chamber, transient gas concentration method is used. A Beckman oxygen analyzer is used with continuous gas sampling of the diffusion source chamber. Theory is presented for diffusion through porous media with no sink or source terms.

Troeh, Jabro and Kirkham. (1982)

The commonly used equations relating the gas diffusion coefficient to air-filled porosity are examined. The commonly used linear $D/D_o = a(E-b)$ and curvilinear $D/D_o = kE^m$ are discussed in terms of their advantages and limitations. A more accurate and general equation is presented, i.e., $D/D_o = ((E-u)/(1-u))^v$. An extensive table of values for the curve fitting parameters, derived from the data available in the literature, is given.

vanBavel. (1954)

A simple straight cylindrical tube inserted into the soil is flushed with nitrogen and the oxygen diffusion coefficient is calculated from the rate at which oxygen diffuses into the cylinder. Charts for computing purposes are given. The physical and mathematical aspects of the method are presented, along with experimental data.

Willey and Tanner. (1963)

Continuous in situ measurement of oxygen concentration of soil-air is accomplished using a temperature-compensated membrane-covered polarographic electrode. A robust design permits sealing in a soil access tube. The time constant is on the order of 0.25 minutes, and the relative error in the measurement is approximately 2%. Geneal design features of the probe and example measurements are presented. A plot of percent oxygen versus time over a six-day period is presented, which shows response to soil surface cracking and rainfall events for a probe 12 inches deep in a silty clay loam.

APPENDIX 5

Glossary of Symbols

APPENDIX 5: GLOSSARY OF SYMBOLS

Parameter	Symbol	S.I. Unit	Commonly Used Unit
Air-filled Porosity	E	-	-
Area	A	m^2	
Concentration of Oxygen in the Atmosphere	C_o	mol m^{-3}	
Concentration of Oxygen in Gas Phase	C	mol m^{-3}	mol L^{-3}
Concentration of Oxygen in Water	C*	mol m^{-3}	
Degree of Water Saturation	S_w	-	
Density (Dry Bulk)	ρ_d	kg m^{-3}	g cm^{-3}, kg dm^{-3}
Density (of Solid Particle)	ρ_s	kg m^{-3}	g cm^{-3}, kg dm^{-3}
Density (of Water)	ρ_w	kg m^{-3}	g cm^{-3}, kg dm^{-3}
Diffusion Coefficient (Effective)	D_e	$m^2 s^{-1}$	$cm^2 s^{-1}$
Diffusion Coefficient (Measured)	D	$m^2 s^{-1}$	$cm^2 s^{-1}$
Diffusion Coefficient in Water	D_o	$m^2 s^{-1}$	$cm^2 s^{-1}$
Dissolution Constant for Oxygen in Water	K_w	-	-
Empirical Constants	a	-	
	b	-	
	u	-	
	v	-	
Flux of Oxygen (Advective)	F_a	mol $m^{-2} s^{-1}$	mol $m^{-2} a^{-1}$
Flux of Oxygen (Diffusive)	F_d	mol $m^{-2} s^{-1}$	mol $m^{-2} a^{-1}$
Hydraulic Conductivity	k	m s^{-1}	cm s^{-1}
Hydraulic Conductivity (Saturated)	k_s	m s^{-1}	cm s^{-1}
Hydraulic Head	h	m	
Mass of Solids	m_s	kg	
Mass of Water	m_w	kg	
Porosity	n	-	
Pressure Head	p_w	m	
Pressure Head at $k = 1/2\ k_s$	p_w*	m	
Rate of Infiltration (discharge)	q	$m^3 s^{-1}$	L s^{-1}, L min^{-1}
Reaction Term in Diffusion Equation	G	mol $m^{-3} s^{-1}$	
Soil Depth	x	m	
Specific Discharge (or Darcy velocity)	v	m s^{-1} ($m^3 m^{-2} s^{-1}$)	
Thickness of Cover	L		
Time	t	s	
Void Ratio	e	-	
Volume (Total)	V_T	m^3	
Volume of Air	V_a	m^3	
Volume of Voids	V_v	m^3	
Volume of Water	V_w	m^3	
Water Content (Mass)	w_m	-	
Water Content (Volumetric)	w	-	